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Evaluating Ozone and Granular Activated Carbon Treatment for Control of Disinfection By-Product Formation for a Central Florida Groundwater Supply

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EVALUATING OZONE AND GRANULAR ACTIVATED CARBON TREATMENT FOR CONTROLLING OF DISINFECTION BY-PRODUCT FORMATION IN A CENTRAL FLORIDA GROUNDWATER SUPPLY

by

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ABSTRACT

A pilot investigation that compared ozone oxidation with an integrated ozone and granular activated carbon (GAC) process for the control of regulated disinfection by-products at the University of Central Florida's water plant located at the Orlando campus has been completed. Treatment effectiveness was measured by monitoring the parameters pH, temperature, non-purgeable dissolved organic carbon (DOC), ultraviolet absorbance at a wavelength of 254 nm (UV_{254}), specific ultraviolet absorbance (SUVA), excitation emission matrices (EEMs) and the associated formation of the DBP chemical groups total trihalomethanes (TTHMs) and haloacetic acids (HAAs). Groundwater that contained an average of 2.5 milligrams per liter (mg/L) DOC and 0.8 mg/L total sulfide was fed to a 15 gram/hour ozone contactor prior to being transferred to two parallel GAC pilot columns, each containing a different coal-based GAC material, either denoted Filtrasorb® (FS-400) or HPC-830 (HPC-830), with an apparent density of 0.54 and 0.36 grams per cubic centimeter, respectively. Stand-alone ozone treatment having an instantaneous ozone demand of 0.82 mg/L O_3 provided a 6.0 mg/L O_3 residual that when held for 30 minutes, followed by the addition of 5 mg/L Cl_2 to represent disinfection, reduced 48-hour TTHM formation by 22 percent, however, increased 48-hour HAA formation by 67 percent. The integrated ozone-GAC process was found to consistently reduce 24-hour and 48-hour TTHM and HAA formation to below regulatory levels through the entirety of the 420 hours of operational run-time. Results for the integrated ozone-GAC process operating at a dose of 7.20 mg/L O_3 both FS-400 and HPC-830 carbon types reached an average of 60% breakthrough for UV_{254} and DOC in the last 1000 bed volumes of the study. Projections with these results provided an estimated 30,000 EBV and 35,000 EBV for the FS-400 and HPC-830 carbon types, respectively, and could be achieved prior to bed DOC exhaustion.

This thesis is dedicated to my friends, loved ones and life mentors.

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LIST OF ABBREVIATIONS

AOC	Assimilable Organic Matter
AN	Abrasion Number
BAC	Biological Activated Carbon
BDCM	Bromodichloromethane
CL	Critical Level
COD	Chemically Oxidized Demand
CT	Contact Time
DBAA	Dibromoacetic Acid
DBCM	Dibromochloromethane
DBP	Disinfection By-Product
DBPR	Disinfection By-Product Rule
DCAA	Dichloroacetic Acid
DI	Distilled
DO	Dissolved Oxygen
DOC	Dissolved Organic Matter
TDS	Total dissolved Solids
EBCT	Empty Bed Contact Time
EBV	Empty Bed Volume
EEM	Excitation Emission Matrices
EPA	Environmental Protection Agency
ESEI	Environmental Systems Engineering Institute
FDEP	Florida Department of Environmental Protection
FP	Formation Potential
GAC	Granular Activated Carbon
GPD	Gallons Per Day
GST	Ground Storage Tank
GWR	Groundwater Rule
HAA	Haloacetic Acid
HAA5	Five Haloacetic Acids
HS	Hydrogen Sulfide
IARC	International Agency for Research on Cancer
LRAA	Locational Running Annual Average
MCL	Minimum Contaminant Level
MRDLG	Maximum Residual Disinfectant Level Goals
NIPDWR	National Interim Primary Drinking Water Regulations
NOM	Natural Organic Matter
OH	Hydroxide
ORP	Oxidative Reduction Potential

OTE	Ozone Transfer Efficiency
PLC	Programmable Logic Controller
PPB	Parts per Billion
PPM	Parts per Million
PSA	pressure Swing Adsorption
PWS	Potable Water System
QAQC	Quality Assurance Quality Control
RAA	Running Annual Average
RPD	Relative Percent Difference
SDWA	Safe Drinking Water Act
SFA	Surficial Floridan Aquifer
SUVA	Specific Ultraviolet Absorbance
SWTR	Surficial Water Treatment Act
TCAA	Trichloroacetic Acid
THM	Trihalomethanes
TTHM	Total Trihalomethanes
UCF	University of Central Florida
US	United States
EPA	United States Environmental Protection Agency
UV	Ultra-Violet
UV_{254}	ultraviolet light absorbance at a wavelength of 254-nm
WL	Warning Level
WTP	Water Treatment Plant

CHAPTER 1. INTRODUCTION

The Safe Drinking Water Act (SDWA) of 1974 authorized the Environmental Protection Agency (EPA) to set national standards to protect the consumers of potable water in the United States and its Territories (US) from anthropogenic and natural contamination, and over time, introduced amendments that sought to enhance the requirements as new health effects and new scientific knowledge became available. One such amendment included the Stage 1 and Stage 2 Disinfectants and Disinfection Byproducts Rule (D/DBPR) that required public water systems (PWSs) to rethink their current treatment and distribution system management strategies. The D/DBPR regulates two classes of DBPs that are suspected carcinogenic contaminants that form as a result of chlorine disinfection processes used to inactivate pathogens in the supplies served to the public. After its promulgation in 1996, the Stage 1 DBPR initially based compliance for TTHMs and HAA5s maximum contaminant levels (MCLs) to be determined by the running annual average (RAA) that averaged four quarterly results of water samples collected at four different locations representing the furthest expanses of a water system's distribution system (EPA, 1998).

However, with the promulgation of the Stage 2 DBPR in 2006, MCL compliance for the same compounds is now calculated based on a locational RAA (LRAA) for each monitoring location in the distribution system (EPA, 2006). This change in enforcement has highlighted regions in PWSs that are prone to producing DBPs, as the formation of the regulated TTHMs and HAAs as they are suspected carcinogens may not be consistent across a given water distribution system. In most cases, potable water transmission pipelines prone to elevated LRAA's are often due to system water age, elevated temperatures, and valve management practices and are as such to more likely to produce elevated DBP content.

In general, the purpose of drinking water treatment is to comply with the primary and secondary standards mandated by the EPA (EPA, 1979). In the state of Florida, the Florida Department of Environmental Protection (FDEP) has been serves as the primacy agency that has the authority to enforce the primary standards established within the federal SDWA Rules for more than 90 contaminants. Secondary standards that ae not considered enforceable by the EPA are in fact enforced by the many state agencies to include the FDEP. Violation of the SDWA provisions can be punitive.

It has been reported by Bush and Richard (1988) that the Floridan Aquifer is one of the major sources of potable water supplies used by municipalities in Florida, Alabama, Georgia and South Carolina, and extends for over an area that approximates 100,000 square miles (Bush and Richard, 1988). It is not unexpected then that the Floridan Aquifer serves as the major supplier of water to most Central Florida potable water purveyors. In 2010, 89 percent of the 2.2 billion gallons per day of the potable water produced by Florida-based utilities was sourced from groundwater pumped out of the Floridan Aquifer (Gerardus, et al., 2015). Notwithstanding the numerous regulated contaminants that may exist within a surface or groundwater supply, some non-regulated chemical constituents that although not regulated may impact TTHM and HAA formation downstream of chlorine disinfection processes and include natural organic matter (NOM), or "precursor" matter, bromide, and total sulfide. When groundwater containing NOM (as measured by total organic carbon) is disinfected with chlorine, DBPs are formed. Also, the presence of bromide in the presence of chlorine and NOM will form brominated DBPs, and depending on specific chemistries, can form bromate (which can occur when ozone oxidation is integrated within the utility's treatment regime). Bromate is also a regulated DBP (EPA 1979b). Also, it is often common practice, although not required, to removed dissolved total sulfide because the chemical

causes a significant chlorine demand during disinfection as well as issues related to taste, odor, and corrosivity. NOM may share the same fate as bromide in a PWS, as under certain conditions organic matter can react with disinfectants to form into halogenated DBPs, such as total trihalomethanes (TTHMs) and haloacetic acids (HAA5s). The TTHMs and HAA5s regulatory MCLs as established by the EPA are delineated at the LRAA and set at 80 parts per billion (ppb) and 60 ppb, respectively (EPA, 2006). Bromate, a regulated DBP that can result from the use of advanced oxidation processes such as ozone, is regulated by EPA at the MCL of 10 ppb.

There are many options that utilities can consider when addressing methods that can lower or eliminate DBPs from forming in water distribution systems that may include (but are not limited to) treatment for the removal of precursors such as TOC and bromide, use of alternative disinfectants, and removal of DBPs after being formed in the disinfection process. For example, TOC can be removed from groundwater supplies using granular activated carbon (GAC), anion exchange, and membrane processes (Wood and DeMarco, 1979; Schaefer et al., 2020; Escobar et al., 2000). . Zhang et. al (2015) also observed that bromide can be removed from drinking water through implementation of granular activated carbon (GAC) in both pilot and bench scale experiments. Krasner et al. (2006) showed that use of alternative disinfectants such as ozone, chlorine dioxide and chloramines can control formation of DBPs in groundwater supplies. The efforts described in this thesis are primarily concerned with research that was performed to evaluate alternative treatment(s) that could be employed by groundwater purveyors to better manage their efforts to comply with the Stage 2 D/DBPR requirements.

The University of Central Florida (UCF) is located near Orlando in western Orange County, Florida. The University owns and operates its own water treatment and distribution system on campus through its Utilities and Energy Services department (referred to as Utility); the water

system is in general comprised of four ground water wells, one 120,000 gallon ground water storage tank (GST) with tray aeration and recirculation appurtenances, and an elevated 200,000 gallon water tower. The Utility distributes water throughout campus to serve its faculty, staff and students.

The Utility has in recent times faced challenges in complying with the requirements set forth by the Stage 2 DBPR. In 2018, the Utility began exploring methods to reduce the formation potential for DBPs within their distribution system internally with their operations staff as well as with the assistance of UCF's Environmental Systems Engineering Institute (ESEI) that aided in preliminary examinations of the existing treatment and distribution procedures and management methods. Projects piloted by the ESEI included implementation of enhancements to the existing tray aerators by modification with spray nozzles and GST recirculation, and the assessment of GAC filtration. Based on the results of the Utility and ESEI studies, it was concluded that a change in the chlorine dosing location and implementation of recirculation piping in the GST would reduce DBPs (UCF ESEI, 2019a). In addition, installation of auto-flushers also remediated DBP formation potentials within the distribution system. These actions were presented at the Florida Section American Water Works Association's conference held at Champions Gate, Florida in 2019 (Shukla and Duranceau, 2019).

Currently, UCF is master planning for future potable water systems to be installed onto the campus within the next 10-years. Based in part on the prior efforts of the Utility and ESEI, it was determined that it would be beneficial to pilot ozone and GAC filtration, which was an expanded concept to the prior stand-alone GAC study already completed. The research presented in this thesis was performed between the fall of 2020 and carried into the spring of 2021, and consisted of exploring the removal efficiency of DBP precursors and further reduction in DBP formation

from a stand-alone ozone process in addition to an integrated ozone-GAC treatment process at the UCF on-campus water treatment plant (WTP). The document will provide information to explain DBP formation as well as formation potentials for TTHMs, HAA5s and organic precursor analysis through the monitoring of dissolved organic carbon (DOC), the absorbance of ultra-violet light at a wavelength of 254-nm (UV_{254}), specific ultra-violet absorbance (SUVA), and pilot-scale process operations data.

CHAPTER 2. LITERATURE REVIEW

Disinfection By-Product Regulation

On November 29, 1979, the EPA promulgated an amendment to the National Interim Primary Drinking Water Regulations (NIPDWR) to control THMs in drinking water (Federal Register, 1979; EPA, 1979). This rule set an interim MCL for TTHMs, defined as the sum of four trihalomethanes, of 0.10 mg/L for community water systems (CWS) serving 10,000 or more people and using a chlorine-based disinfectant. The Stage 1 Disinfectants and Disinfection Byproducts Rule of 1998 (EPA, 1998) reduced the MCL for TTHM to 0.080 mg/L, added MCLs for the sum of five haloacetic acids (HAA5) of 0.060 mg/L, bromate of 0.010 mg/L and chlorite of 1.0 mg/L, and increased the scope of the rule to cover all CWS that disinfect water. Currently the SDWA standards exist for two classes of halogenated organic DBPs, trihalomethanes (THM) and haloacetic acids (HAA), and for two inorganic compounds, bromate and chlorite (EPA, 2007). Additionally, measures based on these contaminants are used to reduce human exposure to DBPs in publicly provided drinking water systems that are encouraged to enhance source water quality, provide infrastructure improvements or other interventions to reduce DBP exposure of consumers in the distribution system.

In 1974, a chemist by the name of J.J. Rook discovered in Rotterdam that post-chlorinated drinking water supplies containing concentrations of NOM higher than 150 ppb were prone to producing halogenated trihalomethanes (Rook, 1974). It is now commonly accepted that DBPs are formed when disinfectants used to inactivate microbial contaminants in water react with materials, primarily organic matter, in the water (Bellar et al. 1974; Rook, 1974; Cedergren et al., 2002; Sadiq and Rodriguez, 2004). Several hundred DBPs in over a dozen chemical classes have been

identified (Woo et al., 2002; Krasner et al., 2006; Richardson et al., 2002). Most commonly, DBPs form when chlorine reacts with naturally occurring organic matter in the source water. The halogens detected included chloroform, bromodichloromethane (BDCM), dibromochloromethane (DBCM) and bromoform, and now are commonly referred to as the four THM species (Rook, 1974). The discovery of halogenated species in chlorinated surficial and groundwater supplies, and the following reports on their potential carcinogenic properties, provided cause for concern in many governments. Rook's discovery of THMs in drinking water led to research on other chemicals formed when chlorine is added to water, and to the health effects of these chemicals. Richardson (2002) identified greater than 600 water disinfection by-products in chlorinated tap water, including haloacetic acids (HAAs). DBP levels are spatially and temporally labile within a distribution system (Rodriguez et al., 2004b). THM levels increase with time after disinfection and therefore with distance from the treatment plant (Chen and Weisel, 1998; Rodriguez and Sérodes, 2001). HAA levels may increase or decrease (Chen and Weisel, 1998; Rodriguez et al., 2004b), depending upon distribution system conditions. Rechlorination at booster stations in the distribution system further increases DBP levels.

On December 16th, 1998, the Stage 1 DBP Rule (DBPR) later established maximum residual disinfectant level goals (MRDLGs) for disinfectants and MCLs for four THMs, two HAAs, chlorite and bromate, in addition to mandates by the EPA for the monitoring, reporting and public notification of the previously stated compounds (EPA, 1998). MRDLGs are not enforceable by law, and act as goals for water purveyors to achieve. Chlorite appears in drinking water when chlorine dioxide is added to the water supply as a disinfectant, and levels can range from 3.2 to 7.0 mg/l depending on the dose of the disinfectant (Michael et al., 1981). Bromate may appear in a drinking water system if the supply contains an elevated concentration of bromide and a strong

oxidizer, such as ozone, is used in the purification process. Because of these operational requirements, potable water purveyors are only required to report chlorite and bromate if the application of ozone or chlorine dioxide as disinfectants are included in the treatment system.

Changes to the MCLGs and MCLs poised in the Stage 1 DBPR were then made with the addition of the Stage 2 DBPR, which was promogulated on January 4, 2006. The new rule aimed to strengthen the reporting and monitoring requirements for DBPs by reducing the peak and average levels of DBPs in drinking water systems (EPA, 2003). This was accomplished through the alteration of the calculations made in determining the compliance of a system from a total system overview to a locational-centric overview, which is more efficient as a 'warning signal' for areas prone to higher formations of DBPs in PWSs (EPA, 2003). The Stage 2 DBPR also included regulation for HAA5s, altering the MCLG for monochloroacetic acid and trichloroacetic acid to 0.07 and 0.20 mg/l, respectively (EPA, 2003). Table 2 displays the MCLs and MCLGs for DBPs outlined in the Stage 1 and Stage 2 DBPR.

Table 2-1: MCLs and MCLGs for DBPs per the Stage 2 DBPR

Regulated DBP	**Stage 1 DBPR**		**Stage 2 DBP**	
	MCL (mg/l)	**MCLG (mg/l)**	**MCL (mg/l)**	**MCLG (mg/l)**
TTHM	0.080		0.080	
Chloroform		-		0.07
Dibromodichloromethane		Zero		Zero
Dibromochloromethane		0.06		0.06
Bromoform		Zero		Zero
HAA5	0.060		0.060	
Monochloroacetic Acid		-		0.07
Dichloroacetic Acid		Zero		Zero
Trichloroacetic Acid		0.3		0.2
Bromoacetic Acid		-		-
Dibromoacetic Acid		-		-
Bromate	0.010	Zero	0.010	Zero
Chlorite	1.0	0.8	1.0	0.8

Disinfection By-Product Links to Health Effects

The classifications of possible human carcinogens come from data that is extrapolated from research on animals that may or may not be relevant to human cancer. DBCM and bromoform are not classifiable, indicating there is no evidence supporting these two compounds as carcinogens, but there is not enough research to classify them as non-carcinogenic (World Health Organization 1993). There is inadequate epidemiological evidence of carcinogenicity in humans for the four compounds. However, in 1991, 1999, and again in 2004, the International Agency for Research on Cancer (IARC) evaluated the evidence of the human carcinogenicity of chlorinated water as well as the by-products it produces (IARC, 2004). Although the extent of the data provided the International Agency for Research on Cancer with insufficient evidence to classify the by-products as carcinogenic, the research served as an impetus for the US Environmental Protection Agency to establish maximum contaminant level goals for several of the by-products, including total TTHM and five HAAs (EPA, 1998).

Disinfectants such as chlorine, chlorine dioxide (ClO_2), and ozone act as strong oxidizers to reactive NOM. Through chemical reactions driven by optimal pH, temperature and contact time, the oxidative properties of post-disinfected waters react with readily available precursors, namely NOM and bromide, to form DBPs; some of which are considered potentially carcinogenic (Chaukura, et al., 2020). The chronic exposure of such DBPs have been linked to higher rates of cancer, neurological disorders, and maternal disadvantages (Nieuwenhuijsen, 2000). Chlorinated THMs are also suspected to induce weight gain and reduce the reproductive and survival rates of offspring of male and female rat populations (Morris et al., 1995). Links between chlorinated THMs and teratogenicity have not been found, however increased doses of such compounds have been related to lower embryo weights and decreases in the survival rate in rate populations

(Ruddick et al., 1983). Smith et al. (1992) discovered that feeding rats DCAA and TCAA, yielded the development of neural tube and craniofacial defects.

Water Quality Considerations

The formation of DBPs in potable water is influenced by natural and anthropogenic factors. Such factors that attribute to DBP formation in potable water include temperature, pH, disinfectant application, sulfide, bromide and NOM.

Disinfection Conditions

The influence on DBP formation by disinfection processes can vary spatially and temporally and are influenced by temperature, pH, and disinfectant application (Clark and Sivaganesan., 1998). In post-chlorinated waters, DBP formations have been observed to increase with increasing pH and temperature (Hua and Reckhow, 2008; Huang et al, 2019). Additionally, the retention time, dose and residual of reactive disinfectants such as ozone and chlorine with water have also been observed to impact DBP formation (Liang and Singer, 2003). Liang and Singer (2003) investigated the relationship between TTHM and HAA5 formation for various disinfectant parameters (such as chlorine retention time and residual) and observed that TTHM and HAA5 formation predominantly occurs within the first hours of disinfectant retention, however as the concentration of disinfectant decreases, the formation also decreases (Liang and Singer, 2003).

Sulfide

Natural sources of dissolved sulfide typically found in the form of hydrogen sulfide (H_2S) in groundwater supplies are derived from the biogenic reduction of dissolved sulfate by aquatic bacteria and through the decomposition of buried organic matter (Rye et al., 1981). Sulfide can

occur in both gaseous and aqueous forms, and such removal of H_2S from a water supply is critical as the contaminant can increase the corrosivity and negatively impact the palatability of potable water (Duranceau et al., 2010). Additionally, the oxidization of sulfide can also influence the turbidity and color of the treated water (Lyn and Taylor, 1992). Existing methods used in Central Florida to remove sulfide from water supplies have included chlorination and aeration. Such treatment processes include the application of strong oxidizers, anion exchange and GAC filtration (Duranceau et al., 2010).

In groundwater, sulfide can occur in three states: H_2S, bisulfide (HS^-) and elemental sulfide (S^0); sulfide (S^{2-}) exists at pH above 12 and is typically not applicable to normal water supplies. The sum of the three states of sulfide is referred to as total sulfide, often reported in mg/l as S^{2-}. Natural sources of groundwater in Central Florida typically occur at neutral pH, so the main fraction of total sulfide removed from the water is in the form of H_2S (Duranceau et al., 2010). Aeration has been used as an effective technology for the removal of hydrogen sulfide. As such, only a portion of total sulfide can be removed through existing treatment processes. In addition, sulfide can reduce strong oxidizers used in drinking water treatment processes. For example, implementation of an ozonation process may be negatively impacted by the dissolved sulfide content, as an increase in the required ozone dose needed to overcome the chemical demand provided by excess sulfide can increase capital costs incurred by the generation of ozone. The chemical demand equation for the reactions of sulfide and ozone are included in Equation 2.1. Per stoichiometry, 4.0 moles of ozone are required to produced 1.0 mole of sulfate (SO_4), however in practice the demand is typically 2.4 mole of ozone per 1.0 mole of SO_4 produced. This delineation from chemical formulation occurs because the applied ozone will decay back into oxygen during treatment, which will also react with sulfide to form sulfate and lower the chemical demand of the water.

$$S^{-2} + 4O_3 + 4H_2O \rightarrow SO_4^{-2} + 4O_2 \quad (2.1)$$

The rate of sulfide oxidation depends on pH and temperature; therefore, the kinetics of sulfide oxidation is locational specific. Additionally, chlorination of sulfide laden waters containing a pH value higher than 3.8 has been observed to produce sulfur turbidity depending on the free chlorine to total sulfide molar ratio, which will further react with free chlorine resulting in an increase to the required chlorine dose and a possible increase to DBP formation (Lyn and Taylor, 1992).

Bromide

If concentrations of bromide in a PWS increase above 0.1 mg/l of bromide is detected in a potable water supply, concern for the implications of brominated DBPs on the health of public consumers must be carefully investigated (Sohn, 2006). Bromide can act in a similar capacity as NOM in serving as a DBP precursor, and under certain conditions form dangerous carcinogens. Bromide can originate in a groundwater supply through saltwater intrusion and previous geological formations (Salameh et al., 2016). Najm and Krasner (1995) studied the effects of bromide and NOM on the production of bromate and cyanogen bromide and found that the effects of bromide were much more significant in DBP formation when compared to those formed from DOC (Najm and Krasner, 1995). Consumption of brominated DBPs also carries a higher risk of negatively impacting human health as compared to chlorinated DBPs, so reduction of the compounds is often targeted in treatment. Direct reduction of bromate can be achieved through pH balance, addition of ammonia (Gunten, 2003), GAC filtration (Siddiqui et al., 1996) and addition of hydrogen peroxide (H_2O_2) (Kruithof et al., 1993). However, the adsorption capacity of GAC for bromate may be significantly lowered if concentrations of chloride or sulfate are present (Mills et al., 1996).

Natural Organic Matter

Natural organic matter (NOM) can impact color of the water feeding the distribution system, contribute to DBP formation and can cause a reduction in dissolved oxygen in the system (Bhatnagar and Sillanpää, 2017). NOM has also been observed to decrease the treatment efficiency of oxidants in processes that employ ozone and chlorine dioxide (Owen et al., 1993). Sources of NOM in a water supply are derived from interactions between the hydrologic cycle, lithosphere, and biosphere (Bhatnagar and Sillanpää, 2017). NOM originating from terrestrial sources is typically composed of hydrophobic compounds, while NOM from aquatic environments (typically deriving from algae) is comprised of hydrophilic compounds (Tak and Vellanki, 2018). As such, the characteristics of NOM will vary based on the majority fraction of NOM in a water supply, resulting in a difference in treatment capacity between select processes depending on the fraction of NOM present (Nkambule et al., 2012).

The fractionation of NOM can be generalized into hydrophobic (humic) and hydrophilic (non-humic) compounds (Tak and Vellanki, 2018). The hydrophilic portion of NOM consists of carbohydrates and proteins, which are of less interest when studying DBPs as they hold less of an impact on their formation (Sillanpää, 2015). However, the hydrophilic portion of NOM does support bacterial growth within a PWS (Karnik et al., 2005). In contrast, the hydrophobic fraction of NOM dominates a major portion of aquatic dissolved organic carbon (DOC) and includes humic and fulvic acids (Owen et al., 1995). These acids are aromatic in structure and are sourced from decayed plants that are resistant to biodegradation but have a high reactivity to chlorine. In addition, hydrophobic fractions of NOM are prone to producing DBPs (Aiken et al., 1992), however little research has been conducted on the correlation between specific NOM fractionation and DBP formation (Kim and Yu, 2005).

Methods to detect and identify aquatic NOM include the analysis for total organic carbon (TOC), dissolved organic carbon (DOC), ultraviolet light absorbance at a wavelength of 254-nm (UV_{254}), fluorescence spectroscopy and assimilable organic carbon (AOC). The EPA assesses NOM type and concentration through analysis of surrogate properties associated with TOC, often reported as concentrations of DOC and UV_{254} absorbance (EPA, 2012). Both DOC and UV_{254} require samples to be filtered through a 0.45 µm filter before measurement can be taken, since both measurements focus on the dissolved fractions of organic matter and suspended media will impact the results. Resulting DOC and UVA_{254} of a water supply can also be interpreted as the specific UV absorbance (SUVA), which can be used to identify the aromaticity and hydrophobicity of organic carbon along with its TTHM formation potential (EPA 2012). Calculation of SUVA is completed through use of Equation 2.2 and interpretation of SUVA values, as provided by the EPA, can be investigated using Table 2-2 (EPA, 2012).

$$SUVA = \frac{UVA_{254}(cm^{-1})*100}{DOC\ (\frac{mg}{l})} \tag{2.2}$$

Table 2-2: SUVA Relation to UVA_{254} Absorbance and TTHM Formation Potential

SUVA Value, $cm^{-1}/(mg/l)$	Matter Fraction	UVA_{254} Abs.	TTHM FP
x < 2	Hydrophobic non-humic matter	Low	Low
2 < x < 4	Hydrophobic non-humic and humic matter	Medium	High
x > 4	Hydrophobic aromatic humic matter	High	High

Source: EPA, 2012

The understanding of aquatic NOM fractionation in water supplies has been researched extensively (Abbt-Braun et al., 2004; Thurman, 1985) and a relatively simple method to its detection includes fluorescence spectroscopy, which can articulate the functional groupings of

organic molecules (Baghoth et al., 2011). Hudson et al. (2007) investigated the behavior of NOM through a review of fluorescence completed on waste, marine and freshwaters (Hudson et al., 2007). Results indicate that fluorescence spectroscopy, primarily excitation emission matrices (EEMs), have potential for a wide application in studies requiring rapid water quality testing (Hudson et al., 2007). EEMs are a three-dimensional spectroscopy method than can be used to characterize aquatic NOM to identify substances that mirror the behaviors of humic matter and proteins (Baghoth et al., 2011). This method of identification can be accomplished through analysis on peaks produced from the resulting EEMs using parallel factor analysis, which has a higher predictability of NOM fractions than UVA_{254} (Baghoth et al., 2011). Analysis on EEMs can lead to the understanding of NOM through observations on its five regions of interests, of which can be observed in Figure 2-2.

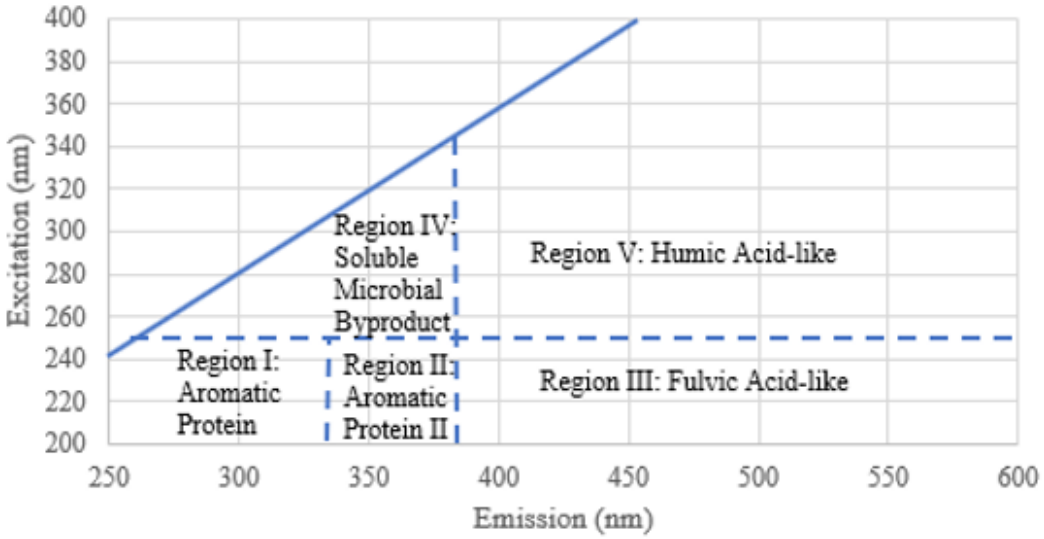

Figure 2-1: Excitation-Emission Matrix Regions for Organic Species

Alternative Methods to Reduce DBP Precursors

Prior research has sought to reduce the formations of chlorinated DBPs, which can be achieved through the reduction of constituents that act as DBP precursors in aquatic environments. Rook (1976) utilized a conventional treatment, carbon adsorption and ozonation train to investigate the removal of organic precursors. Samples dosed with 8 mg/L O_3 for two minutes prior to chlorination produced 50% fewer halogens compared to samples that were not ozonated (Rook, 1976). However, samples that were dosed with 2 mg/L O_3 were observed to harbor a lower efficiency in halogen reduction (Rook, 1976). This would suggest that ozone can reduce the formation potential of halogens at high doses, however the process may require additional processes downstream to assist in further treatment of organic precursors, such as coagulation or GAC filtration if using decreased ozone doses. Water purveyors must compare capital and operational costs of elevated doses of ozone (as production is historically expensive) with decreased ozone in conjunction with downstream treatment.

Treatment processes to remove DBP precursors from source waters include convention treatment methods, ozonation, adsorption and membrane filtration. Treatments investigated in this work include oxidation through ozonation and adsorption through GAC and BAC. The installation of such units and operations set forth to conform with regulation posted by government agencies, with goals to improve water quality and protect public health.

Ozone

Ozone is a strong oxidizer that has the capacity to alter NOM into a more biodegradable form of organic media, which is often reported as assimilable organic carbon (AOC). The relationship between the rate of NOM alteration and biodegradation has been observed to increase with ozone

dose (Huang and Chen, 2004). Research on the interactions between the application of ozone on source waters of different qualities were investigated by Park et al. (2000), who concluded that ozonation was effective in AOC removal. Ozonation is predominantly used in Europe as a disinfectant, as salt reserves that are required to produce the disinfecting chemical chlorine are less available. The production of ozone on-site is required if ozonation is to be included within a system process. As the process can be energy intensive, it may accrue high operation and maintenance (O&M) costs. This may become problematic if the required ozone dose is high, as additional voltage would be required to sustain the elevated dose.

Drinking water applications for ozone in the United States began in the early 1900's, where its capabilities in removing unpalatable characteristics of water afflicting its taste, odor and color were used (Rice, 1999). Reports from the U.S War Departments Surgeon General dictate that the U.S. military researched the practicality of ozonation during wartime in 1909 at Fort Niagara, NY (Loeb et al., 2012). Soon after, the US military abandoned the idea for ozone as an alternative to chlorine and iodine, as ozonation was costly and required a constant source of electricity (Loeb, 2012). In parallel, various drinking water plants around the Great Lakes region championed processes including ozonation for taste and odor control. Ozonation processes in the region were soon replaced as the capabilities of ozone from an engineering aspect had not yet caught up to the advancements in ozonation science and would not be reintroduced in the United States until 1940 where an ozone process was installed for taste and odor control in Whiting, ID (Loeb, 2012).

In 1986, promulgation of the SDWA adopted the *CT* principle to modern drinking water treatment processes which mandated that treated waters must undergo required levels of disinfection in terms of contact time and concentration of disinfectant for the inactivation of microorganisms. The disinfectant properties of ozone warrant the compound a low CT, as ozone requires both a low

dose and contact time to operate as compared to other disinfectants. In the 21st century, ozonation in the United States is primarily used as a pre-treatment method for raw water transmission lines to protect the pipelines from biological growth and to increase the performance of conventional treatments such as coagulation or GAC filtration.

Ozone is usually generated via photochemistry, electrolysis, or corona discharge (Silva and Jardim, 2006). When ozone is produced through corona discharge, concentrated oxygen is produced from ambient air and flowed through an electric discharge that converts the stream into ozone (Espei et al., 2001). The reactions between the electrode and oxygen to produce ozone is found in Equation 2.4, Equation 2.5, Equation 2.6, and Equation 2.7.

$$O_2 + e^- \rightarrow O + O + e^- \quad (2.3)$$

$$O_2 + e^- \rightarrow O_2^* + e^- \quad (2.4)$$

$$O + O_2 + M \rightarrow O_3 + M \quad (2.5)$$

$$O_2^* + O_2 \rightarrow O_3 + O \quad (2.6)$$

As the electric discharge bombardes the oxygen molecules (O_2) with electrons, the oxygen becomes excited (O_2^*) and free oxygen molecules (O) are produced, as displayed in Equation 2.3 and Equation 2.4. Ozone is then generated from the reactions between the O, O_2 and a catalyst (M), as seen in Equation 2.5, and the reactions between O_2^* and O_2, as displayed in Equation 2.6. Ozone will also degrade back into O_2, and the relationship has been observed to increase with increasing temperature (Espei et al., 2001). Ozone is then contacted with a flow, typically in a vacuum produced by the liquid upon the point of gaseous injection and made aqueous. The solubility of ozone during this exchange can be completed through mathematical quantification

and application of diffusivity laws. As a general guideline, the solubility of ozone follows Henry's Law, as seen in Equation 2.7.

$$Y = H * X \tag{2.7}$$

Where, Y is the pressure of substance over the fluid in atmospheres (atm), X is the molar fraction of the gaseous solute in liters per mole (l/mol) and H is the Henry's constant in atmospheres per liters per moles (atm/l/mol).

The solubility of ozone can also be calculated through the Bunsen Adsorption Coefficient, which is displayed in Eq. 2.9.

$$Cs = \beta * M * P \tag{2-8}$$

Where, C_s is equal to the concentration of dissolved gas (Pa*kg/m^3), B is the Bunsen adsorption coefficient (unitless), M is the density of the gaseous solute (kg/m^3) and P is the partial pressure in Pascals.

Analytical models that estimate the solubility of ozone in liquid solvents also include Regular Solution theory (Scovazzo et. al, 2004), the Soave-Redlich-Kwong model (Li et al., 2001) and Scaled Particle theory (Mandell and Reiss, 1975). Ionic strength, temperature, pH, ozone partial pressure, gas flow rate and liquid flow rates also influence the level of ozone solubility, as shown in Table 2.3.

Table 2-3: Influence of Parameters on Ozone Solubility

Parameter	**Influence on Ozone Solubility**
Ambient Air Ozone Concentration	Increases with increasing ambient ozone concentration.
pH	Increases with decreasing solvent pH.
Air Pressure	Increases with increasing air pressure.
Water Temperature	Increases with decreased solvent temperature.
Air Temperature	Increases with decreasing air temperature.
UV Light	Increases with excess UV light.
Number of Solutes	Increases with a decrease in concentration solutes.

The solubility, or mass transfer, of ozone from a gas to a liquid state can be modeled through its three stages of diffusivity: (1) Diffusion of ozone across a gas/liquid phase, (2) Dissolving of ozone into a liquid, (3) Diffusion of ozone into a liquid and the process of mass transfer can be viewed in Figure 2.3 (Berry et al., 2017). Diffusion from a gas to a liquid is determined by physical properties, mechanical turbulence, and difference in concentrations across the transfer surface. The use of non-porous polymetric membranes as contactors for ozonation processes have been observed to increase the mass transfer efficiency as membranes can increase the surface area per volume of the design; therefore, increasing the gas flow and liquid volumes allowed for the effluent gas stream to be recycled back into the system process (Berry et al., 2017). Mass transfer efficiency is an important parameter when calculating the applied dose of an ozone system. To further discern

the feasibility of an ozone process, parameters such as applied dose of ozone and understanding of ozone kinetics after its application are required. The applied ozone dose equation is shown in Equation 2.9.

$$AOD\,\frac{g}{h} = \frac{OD\left(\frac{g}{l}\right)}{OTE\ (\%) * Q\left(\frac{l}{h}\right)} \tag{2.9}$$

Where, AOD is the actual ozone dose in grams per hour (g/h), OD is the ozone demand in grams per liter (g/l), OTE is the ozone transfer efficiency in percent (%) and Q is the liquid flow of the process in liters per hour (l/h).

The determination of an applied dose of ozone can also be completed through stoichiometric evaluation, which requires knowledge of the reducing agents and the resulting residual concentration of ozone. Such chemically oxidized demand (COD) equations are included in Equation 2.10 and Equation 2.11. The ozone demand of sulfide (as HS^- and H_2S) and iron are reported to be as low as 2.4 moles of ozone per mole of sulfate formed and one mole of ozone per two moles of oxidized iron formed.

$$2Fe^{+2} + O_3 + H_2O \rightarrow 2Fe^3 + O_2 + 2OH^- \tag{2.10}$$

$$S^{-2} + 4O_3 + 4H_2O \rightarrow SO_4^{-2} + 4O_2 \tag{2.11}$$

Iron may complex with organics (namely humic acids) in a supply and thus require higher amounts of oxidants and longer contact times to completely precipitate (Reckhow et al., 1991). Portions of NOM from a groundwater supply react differently when oxidized by ozone, which causes the resulting formations of DBPs to vary (Molnar, et. al, 2012). Complete oxidation of NOM into carbon dioxide (CO_2) is typically not encouraged as sufficient ozonation of NOM can be achieved before the NOM has been mineralized (Hoigné, 1998). Win et. al (2000) researched the interactions between ozone and NOM from a brown water lake supply and observed that

biodegradability of the NOM improved with an increased oxidation intensity (Win et al., 2000). However, in samples that were "mildly" oxidized (i.e. 5-min ozone contact time), the biodegradability was unaffected (Win et al., 2000).

Ozonation prior to biological filtration of source waters containing favorable pH, DOC and temperature has also been observed to increase microbiological activity in conventional filters, enhancing the level of biodegradability of DOC (EPA, 1999). When NOM is degraded, its apparent molar size is reduced, generally with the formation of carboxylic acids, which improves its removal efficiency through processes that are designed downstream of ozone such as GAC filtration or conventional treatment. Additionally, an increase in the HAA concentration due to presence of hydrophilic NOM has also been observed (Chowdhury et al., 2008). Epoxides, organic peroxides and aldehydes are also formed from ozonation processes (Can and Gurol, 2003). The mechanisms for aldehyde production post-ozonation are not well understood, however such production has been found to be dependent on pH, ozone dosage, NOM fractionation and alkalinity (Can and Gurol, 2003). Very few studies have focused on the impacts of ozone dose and retention time when studying the formation of aldehydes, namely formaldehyde, and a better understanding of aldehydes may assist in the reduction of such species when ozonation is installed into potable water systems.

Granular Activated Carbon

Removal of contaminants through use of commercial adsorbents can be an efficient and cost-effective means of potable water treatment (Iriarte-Velasco et al., 2008). Adsorption is the accumulation of mass onto a surface and include interactions between the adsorbate (constituent) and adsorbent (carbon). Bromate, bromide, NOM, chlorine, and other compounds that impact the taste and odor have shown to be successfully removed using activated carbon (Zhang et al., 2014;

Matilainen et al., 2010; Kim and Kang, 2008; Duranceau et al., 2010). The removal of NOM also reduces the formation potential for DBPs, so the option is often pursued when DBP reduction is targetted (Rook, 1976). In 1786, Scheele was the first to observe the abilities of charcoal as an adsorbent in a liquid-phase (Sontheimer et al., 1988). Soon after Scheele's discovery, Lowitz determined that charcoal could also improve the palatability of water (Sontheimer et al., 1988). However, it would not be until the nineteenth century where the Swedish chemist Von Ostreijko commercialized activated carbon with two patents in 1900 and 1901, which covered the development of activated carbon using carbon dioxide and metal chlorides (Sontheimer et al., 1988).

Currently, there are numerous corporations that hold patents regarding the manufacturing and design of activated carbon. Activated carbon can be categorized as pelletized carbon, granular activated carbon (GAC), powdered activated carbon, coconut shell, lignite coal, wood, and bituminous coal. Using these ingredients, corporations have also engineered activated carbon product lines that have been observed to effectively treat potable water (Marais and Ncube, 2018). Companies such as Calgon Carbon (Calgon) have designed different carbon types that are used worldwide in potable water treatment. Commercial lines of activated carbon designed and marketed by Calgon include the Filtrasorb, OLC, Centaur and HPC series. During the design of a GAC process, it is recommended that multiple carbon types be piloted to determine the best fit caron type for the existing water source. This would be determined through the analysis on the breakthrough of constituent (namely NOM) and eventual exhaustion of carbon after extended use. Exhaustion of carbon would be concluded when the effluent concentration of constituent equaled that of the influent concentration of constituent.

The selection and capacity of adsorptive media can vary by the quality of raw water and level of pretreatment before the process (Babi et al., 2007). Factors that inhibit GAC adsorptive capacity include loss of adsorptive sites due to residence of other contaminants, biological growth, pH, temperature, and adsorptive kinetics including the hydraulic loading rate and carbon size (Speth and Miltner, 1998). There is a direct relationship between the size of the contaminant and the propensity for van der Waals forces to contribute to the adsorption potential of a particle (Sontheimer et al., 1988). Van der Waals originate from the electrostatic interactions between molecules that do not attract. As such, the surface chemistry of the absorbent is integral in providing a sufficient adsorptive surface and thus effective removal.

Additional methodologies used to study the properties of engineered carbon types include pH of point of zero charge, total HCl and NaOH uptake, and elemental analysis using inductively coupled plasma atomic emission spectroscopy (Cheng, Dastgheib and Karanfil, 2005). Designing for the applications of absorbents in real-world situations can also be determined through chemical breakthrough studies, where columns of carbon adsorbents in bench and pilot settings are subject a flow, typically from a natural water source, and its contaminant removal efficiency is monitored over the piloting period. Breakthrough of the carbon columns is measured through the amount of contaminant exiting the absorbent as compared to the concentration of the contaminant entering the adsorbent. The equation for the measurement of breakthrough is included in Equation 2.12. As the duration of column piloting proceeds, it is expected that the removal capacity of the adsorbent will decrease. This interaction has been studied by multiple researchers with goals of understanding GAC reduction of NOM, DOC, TTHM and HAA5 for design and scaling purposes (Kim and Kang, 2008; Dastgheib et al., 2004).

$$Breakthrough = \frac{C}{C_o} \quad (2.12)$$

Where, C is the concentration of the contaminant in the effluent (mg/l) and C_0 is the concentration of the contaminant entering the adsorbent system.

In 1976, Rook sought to understand the reduction of organic precursors in chlorinated waters through GAC filtration to reduce DBP formation. Rook observed that throughout the lifetime of the adsorptive process, the GAC remained to be effective in reducing larger chlorinated molecules from the effluent stream and further reduce the formations of halogenated species (Rook, 1976). Dastgheib et al. (2004) researched the removal of DOC by GAC filtration that had been enhanced with high-temperature helium, ammonia, and iron-impregnation treatments of coal-based and wood-based carbon types. After altering the surface chemistry of the adsorbents, an increase in DOC removal of water sourced from Myrtle Beach, SC was observed (Dastgheib et al., 2004).

Integrated Treatment

The combination of an ozonation and GAC treatment process has found much use in areas where requirements preventing their individual uses prevents such cases from occurring. Ozonation is effective at degradation certain organics, such as humic substances, however it also proves to be in-effective treating non-humic substances. If left untreated, these compounds can then continue to form DBPs within a distribution system if further treatment is not present. GAC can also efficiently remove NOM from a supply, however if the carbon exhausts quickly, then the user may incur high costs associated with carbon replacements (Lou et al., 2014). Huang and Chen (2004) assessed the effectiveness of ozone and GAC treatment on removing AOC from groundwater localized in Sha-Lu, China, and a correlation was observed between ozonation followed by GAC filtration and a resulting high removal capacity for AOC. Chang et al. (2002) also assessed an

integrated ozone and GAC treatment process to determine the impact of ozone dosage on the subsequent GAC adsorption capacity and determined that the adsorption capacity for humic acids were improved at elevated doses up to 6.0 mg/l O_3. However, the increase in solubility after ozonation resulted in a decrease in affinity of the organics with GAC, resulting in rapid breakthrough to occur.

In this work, an integrated ozone-GAC pilot was evaluated to reduce DBP precursors and subsequent DBP formation potential in the distribution phase of potable water treatment. The pilot was operated in a stand-alone ozonation process, which oxidized NOM at various concentrations of ozone, and an integrated ozone-GAC process which operated at a minimal residual of ozone and enlisted GAC adsorption through two carbon pilot columns in parallel.

CHAPTER 3. EXISTING CONDITIONS

The information presented in this chapter reviews the existing conditions of the UCF groundwater wells and distribution system as well as describe prior research completed by the UCF Utility and ESEI to control DBP formation. The on-campus WTP serves a main campus comprised of 43,103 full-time equivalent population, in addition to one facility off campus that holds 1,000 people when fully staffed, providing a total population served as 44,103. UCF is the largest university by enrollment in Florida and one of the largest universities in the nation. UCF distributes approximately 300 million gallons of potable water per year to approximately the students, faculty, and staff that attend the university for work and study. The PWS is composed of four groundwater wells, a 120,000 gallon GST fitted with tray aerators for hydrogen sulfide and carbon dioxide removal, a 200,000 gallon elevated storage tank (EST), and the ability to add bleach for disinfection downstream of the tray aerators. A schematic of UCF's treatment process is presented in Figure 3-1 and the location of the UCF campus and WTP site are included in Figure 3-2.

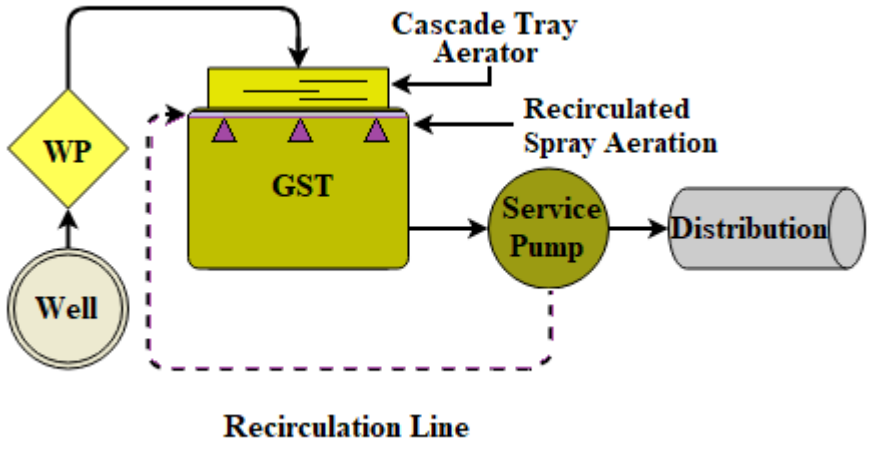

Figure 3-1: Existing UCF WTP Process Schematic

Figure 3-2: Locations of the UCF Orlando Campus (boxed in gold), WTP (circled in yellow) and Well Field (boxed in green)

Existing Groundwater Conditions

Prior analysis on the UCF groundwater supply to determine its characteristics and quality were completed prior to the research here-in by UCF ESEI, the results of which are included in Table 3-1 and Table 3-2.

Table 3-1: Water Quality from UCF Groundwater Supplies (Sampled 7/16/2020)

Parameter	**Well 1**	**Well 2**	**Well 3**	**Well 4**
pH	7.7	7.5	7.5	7.7
Temperature (°C)	24	24	24	25
Conductivity (mS/cm)	360	1150	1240	480
Total Dissolved Solids (mg/L)	260	810	880	350
Turbidity (NTU)	0.14	0.56	0.17	0.26
Total Sulfide (mg/L)	1.3	0.84	0.87	1.90
UV-254 (cm^{-1})	0.073	0.084	0.084	0.068
DOC (mg/L)	2.4	2.7	2.7	2.3
SUVA (L/mg/m)	3.1	3.1	3.1	3.0

Table 3-2: Inorganic Water Quality from UCF Wells 3 and 4 (Sampled 1/22/2019)

Parameter	Well 3	Well 4
Aluminum (mg/l)	< 0.005	< 0.005
Sulfate (mg/l)	2.9	3.9
Bromide (mg/l)	< 0.005	< 0.005
Fluoride (mg/l)	0.26	0.48
Chloride (mg/l)	10	10
Phosphate (mg/l)	1.5	1.3
Alkalinity (mg/l as $CaCO_3$)	150	140
Iron (mg/l)	0.018	< 0.005
Magnesium (mg/l)	7.2	1.3
Calcium (mg/l)	51	42
Silica (mg/l)	11	10
Sodium (mg/l)	5.2	5.3

Source: UCF ESEI REPORT (2019a)

The water quality for each groundwater well varies: well 1 and well 4 contain lower concentrations of total dissolved solids (TDS) and DOC, conductivity and UV_{254}, and higher concentrations of total sulfide and pH as compared to well 2 and well 3. The SUVA values for the four UCF groundwater wells would also indicate that the NOM within the supply contains a mix of humic and non-humic matter, as the values range between 2 L/mg/m and 4 L/mg/m (ESEI, 2019*)*. The source water can also be characterized by a low level of inorganic substances, where the most prevalent of such inorganics include calcium and alkalinity. The bromide content in the UCF groundwater was observed to be below the minimum detection limit at less than 0.005 mg/l, so possible threats issued by the formation of brominated DBPs in the UCF distribution system are expected to be low. DBP experimentation also completed by UCF ESEI in 2019 to analyze for the

potential formations of TTHMs and HAA5s by the groundwater supply under worst-case conditions after aeration, chlorination, and 168-hours of incubation at 30°C can be observed in Table 3-3.

Table 3-3: DBP Formation Potential for the UCF Groundwater Supply

Well No.	Chlorine (mg/L CL_2)		TTHM (µg/L)		HAA5 (µg/L)	
	Dose	168-hr Residual	MCL	Projected 168-hr Formation	MCL	168-hr Formation
1	9	1.50	80	230	60	82
2	9	0.76	80	310	60	92
3	10	0.90	80	290	60	83
4	10	0.61	80	280	60	82

Source: UCF ESEI REPORT 2019a

The chlorine dose required to overcome the chemical demand of the aerated groundwater and maintain a residual between 0.1 mg/l Cl_2 and 1.5 mg/l Cl_2 after incubation were 9 mg/l Cl_2 and 10 mg/l Cl_2. These doses also resulted in the projected TTHM and HAA5 concentrations of approximately 280 ppb and 85 ppb, respectively. These potential formations of DBPs observed in the UCF groundwater exceed the MCLs standardized by the EPA for either contaminant, thus calling for a need of remediation on DBP precursors control in the UCF system to reduce such formations to levels presumed as safe for public health.

On July 29, 2020, approximately 15 gallons of UCF groundwater was transported from UCF to Guardian Manufacturing Laboratories (2750 Dillard Rd, Eustis, FL 32726). Bulk water aliquots were dosed with ozone to achieve specified concentrations of transferred ozone (often remarked as ozone residual in mg/l O_3) for demand and decay studies. The purpose of testing with the ozone manufacturer/supplier (Guardian) was to determine the instantaneous ozone demand and decay,

along with the half-life, of UCF's groundwater per industry standards. However, it is to be noted that the following results do not account for total sulfide present in the source water as aliquots were held in storage for an extended duration before demand and decay experimentation was completed. Displayed in Table 3-4 are the water quality results from such testing.

Table 3-4: Groundwater Quality Characteristics

Sample ID	**Raw Groundwater Sample**	**Transferred Ozone Dose**		
		0.5 ppm	**1.0 ppm**	**1.5 ppm (Decay Test)**
TOC (mg/L)	2.0	2.3	2.2	2.1
Dissolved Oxygen (ppm)	7.7	8.0	8.7	9.3
Temperature (°C)	25	25	25	25
Bromide (µg/L)	22	57	31	44
Bromate (µg/L)	N/a	2.5*	2.5*	2.5*
Total ozone dosage (mg/L O_3)	N/a	5.0	6.5	N/a[2]
Instantaneous Demand (mg/L O_3)	N/a	0.5	0.84	0.82
Half-life (min)	N/a	N/a	N/a	1.23

*Minimum Detection Level (MDL) for bromate.

[2]: The total ozone dosage of the 1.5 ppm transferred ozone dose was not recorded.

Results from the ozone demand and decay tests indicated that a transferred ozone dose of 1.5 mg/l O_3 was the most suitable dose to calculate the instantaneous ozone demand and half-life of the UCF groundwater. Displayed in Figure 3-3 and Figure 3-4 are the resulting ozone residual vs time curve and linearized ozone residual vs. time curve used to calculate the instantaneous demand and half-life for the aliquot after application of 1.5 mg/l O_3 residual.

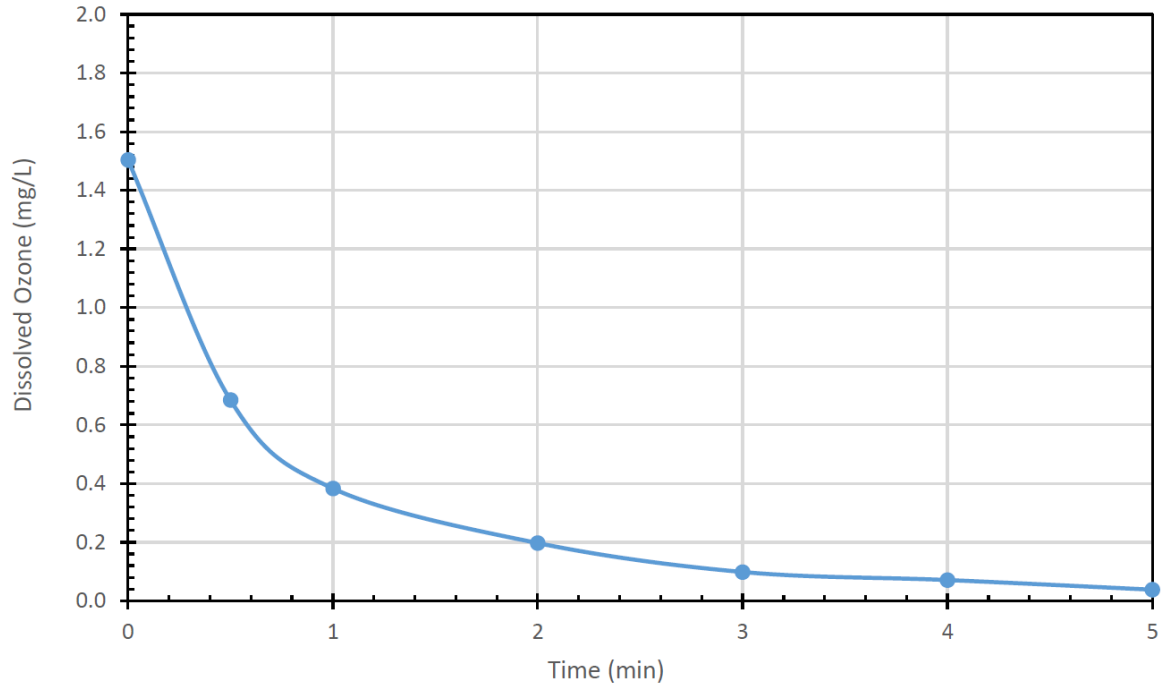

Figure 3-3: Dissolved Ozone as a Function of Time

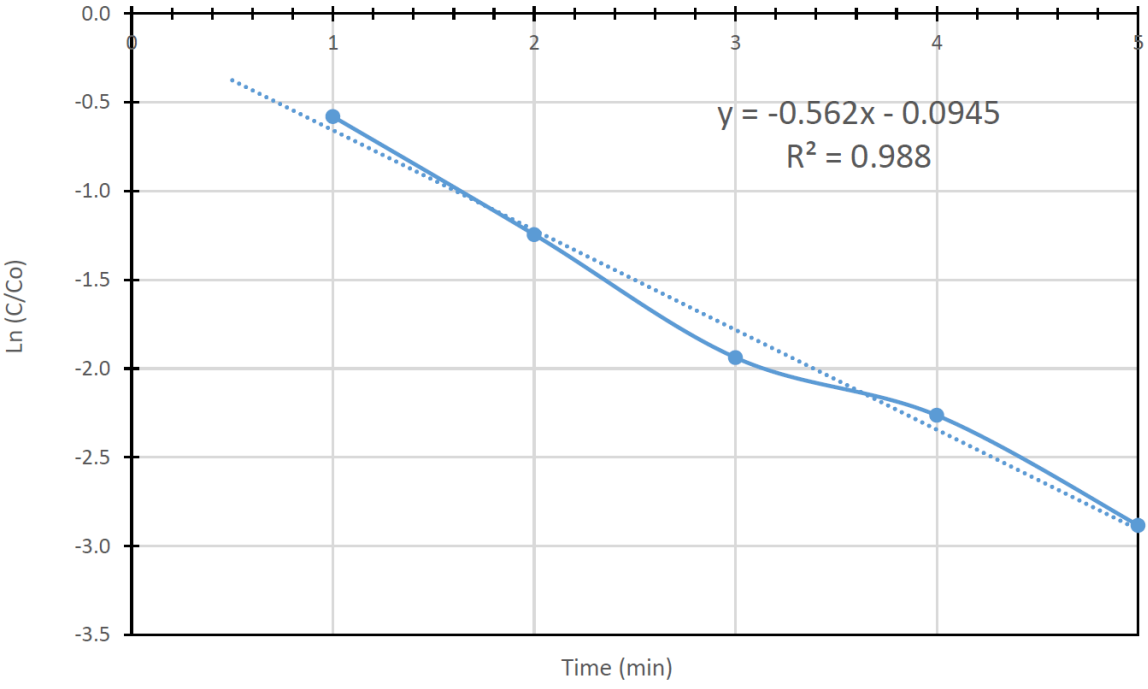

Figure 3-4: Linearized Dissolved Ozone as a Function of Time

The instantaneous demand for this trial was 0.82 mg/L O_3 displaying a well-formed decay curve with a correlation coefficient of 0.988. The slope of the natural log of the decay curve was calculated to be -0.562 mg/L/min with a correlation coefficient value of 0.988, which correlates to a half-life of 1.23-min. As such, the dosage required to satisfy the ozone demand of UCF groundwater and achieve 1.0 mg/l O_3 residual under laboratory conditions would be approximately 6.5 mg/l O_3. However, the realistic ozone dose may change due to demand incurred from H_2S and other variations in groundwater quality.

Existing Potable Water System Conditions

Locations in the UCF PWS that are at a higher risk of DBP formation include the Barbara Ying Center, the Bounce House, sections of Greek Row, Siemens, and Aurora drive. The UCF PWS also has a highly variable demand which is influenced by events such as football games, graduation events, and holiday breaks, so PWS DBP formation varies seasonally and locationally. Sections of the UCF PWS locations vulnerable to higher DBP formation content occur the far reaches of the distribution system, which includes the Barbara Ying Center, Siemens, Greek Row and Arena, as displayed in Figure 3-5.

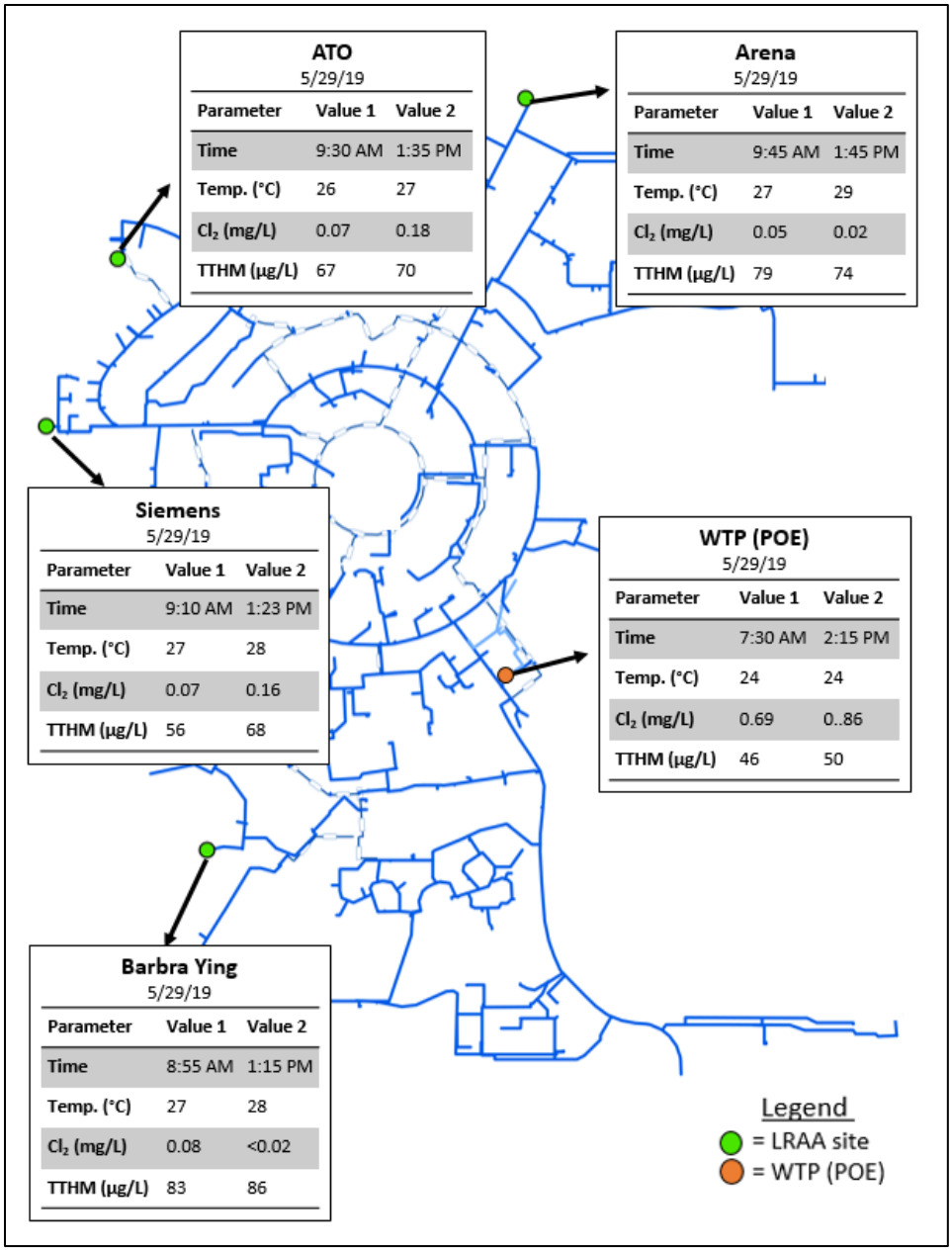

Figure 3-5: DBP Formations at Vulnerable Sections of the UCF PWS

Source: UCF ESEI REPORT 2019a

On May 29th, 2019, concentrations of TTHMs in potable water exiting the UCF WTP were observed to be 46 ppb in the morning and at 50 ppb in the evening, and potable water at one of the ends of the distribution system exceeded the MCL for TTHMs at a concentration of 86 ppb.

Prior Research

UCF Utilities has sought to promote their water system through master planning of future additions to current treatment processes, with aims to minimize the formation of DBPs throughout the entire PWS. In 2019, the UCF PWS failed to comply with EPA's TTHM MCL at one section of the system located at the Greek Residence on campus that yielded a TTHM concentration of 91 ppb, which exceeded the 80 ppb MCL per UCF's consumer compliance report (UCF, 2020). Prior research investigating DBP formation potential performed by ESEI documented that the four groundwater wells when dosed with chlorine exceeded the EPA's MCL of 80 ppb for TTHMs in less than eight hours and the HAA5 MCL of 60 ppb within 168 hours. From 2019 to 2020, UCF Utilities sought to promote their near-term DBP compliance through enhancing their understanding of current conditions in their system through DBP screening and studies on the efficacy of auto-flushing and GST recirculation, spray aeration and tray aeration (ESEI, 2019a). Additional research was also undertaken to evaluate GAC as a stand-alone system using pilot-scale equipment to determine the removal efficiency of DBP precursors from the groundwater supply between mid-April and mid-June 2019. Two GAC types, FS-400 and Centaur 12x40, were fed by the raw influent line from the wells. DOC and UV_{254} of the pilot column effluent were monitored as the DBP precursors of interest and their associated TTHM and HAA5 formations were analyzed to determine the effective treatment potential of the carbon columns in adsorption and biological modes. Initially, the GAC columns were operated as a stand-alone method of treatment, however the columns expended quickly and after 10-days both carbon columns had exhausted and entered the mode of biological removal (ESEI, 2019a). Operation of the columns in biological mode proved to reduce the formation of DBPs by approximately 15%, so the columns would be required to operate in adsorption mode to promote proper DBP reduction, however the

option proved to be financially burdensome to the Utility as the carbon would need to be replaced often so neither option was chosen (ESEI, 2019a). As the stand-alone process has proved to be ineffective, the Utility began to research other options of DBP precursor removal; eventually leading to the investigation on the effectiveness of an integrated ozone-GAC process and stand-alone ozonation process treatment study to be conducted.

CHAPTER 4. METHODS AND MATERIALS

Included in this chapter are the experimental plan, methodologies and materials employed to develop and monitor the presented treatment processes. The controlled operation of either process was accomplished through the development of a pilot at the UCF WTP with capabilities for ozone and GAC treatments. The determination of treatment effectiveness for both processes was measured through the impact on NOM fractionation and formation of DBPs. The impact of the treatment processes on NOM fractionation was determined through the monitoring of DOC and $UV_{254,}$ and calculation of SUVA for both processes, coupled with analysis completed to determine the fluorometric behavior of the raw and ozonated waters. Sampling from the pilot also underwent DBP formation analysis, where the concentrations of TTHMs and HAA5s at certain periods of incubation were extracted.

Water Quality Monitoring and Experimental Procedures

Samples taken from the pilot underwent analysis for water quality parameters as shown in Table 4-1, excluding the analysis procedures for fluorometric behavior analysis which are included in the *ORGANIC COMPOSITION DETERMINATION* section of this chapter. The methods used originate from *Standards and Methods for the Examination of Water & Wastewater 20th Edition*, EPA Standard Methods and HACH Standard Methods (Baird et al., 2017). Methods to the calibration of certain equipment are also included in Table 4-2. Upon their arrival at UCF Laboratories, samples were held for up to four-days after initial sampling in a refrigerator at 4°C. Sampling for DBP formation analysis was completed using 1-gallon and 4-gallon plastic totes and sampling for metals and carbon analysis was completed using 250 mL and 500 mL plastic bottles. Sampling for every other method of analysis completed in the following studies were completed

using 125 mL and 250 mL amber bottles. Collection of water samples from the pilot occurred at the following four sampling ports: (1) Influent line connected to the groundwater supply, (2) Ozone skid contact tank, (3) Downstream from the FS-400 pilot column, and (4) Downstream from the HPC Maxx (HP-830) pilot column. Prior to sampling from the ozone skid and GAC columns, an equivalent of three times the total volume of the pilot of water was flown through the system to promote sampling quality.

During the integrated ozone and GAC study, samples for UV_{254} and DOC were taken every morning after 30-minutes of operation from each port of the pilot. Additional water quality parameters, such as turbidity, pH, temperature, dissolved oxygen (DO), bromide, sulfate, conductivity, oxidation-reduction potential (ORP) and alkalinity were monitored at the pilot during field trips conducted at a frequency of 1-3 days a week over the entirety of the study. Samples for iron, magnesium and calcium were taken three times over the study; once in November, December, and January. At the end of the study, carbon was removed from the top and bottom 6-inches of both columns and shipped to Calgon Carbon Company (Moon Township, PA) to quantify the particle distribution, abrasion number, and iodine number of the activated carbon after its extended use.

The stand-alone ozonation study was completed in duplicate and water quality samples collected during the study were sampled from the groundwater influent line and ozone skid sampling ports of the pilot. Water quality parameters of interest monitored during this study were DOC, UV_{254}, SUVA, ORP, turbidity, pH, temperature, conductivity, ozone residual concentration and formation of DBPs after chlorination, with a primary interest on TTHMs. HAA5s were also monitored during the first trial of the stand-alone ozonation study.

Table 4-1: Methods and Equipment for Water Quality Analysis

Test Location	Test	Method	Equipment Description	Method Detection Level	Preservation Technique	Holding Time
Field	Conductivity	SM: 2510 B. Laboratory Method	HACH HQ40D Conductivity Probe	0.01 µS/cm	N/A	Analyze immediately
	Ozone (Residual)	HACH Method 8311	HACH DR2800	0.01 mg/l – 1.50 mg/l	N/A	Analyze Immediately
	Dissolved Oxygen	YSI Dissolved Oxygen Meter Method	YSI Pro 20 Galvanic DO Probe	0.01 mg/l	N/A	Analyze Immediately
	pH	SM: 4500-H+ B. Electrometric Method	HACH HQ40D pH and Temperature Probe	0.01 pH units	N/A	Analyze immediately
	Sulfide	HACH Method 8131	HACH DR2800	0.01 mg/L	N/A	Analyze immediately
	Temperature	SM: 2550 B. Laboratory and Field Methods	HACH HQ40D pH and Temperature Probe	0.1 °C	N/A	Analyze immediately
	ORP	SM: 2580 B.	HACH HQ40D ORP Probe	-2000 to 2000 mV	N/A	Analyze Immediately
	Turbidity	SM: 2130 B. Nephelometric Method	HACH 2100N Laboratory Turbidity Meter	0.01 NTU	N/A	Analyze immediately
UCF Laboratory	Alkalinity	Standard Methods (SM): 2320 B. Titration Method	Sulfuric Acid Burette Titration	5 mg/L as CaCO3	Refrigerate at 4°C	14 days
	Calcium	SM: 3120 B. Inductively Coupled Plasma (ICP) Method	ICP Spectrometer - Perkin Elmer Avio 200	0.01 mg/L	2% nitric acid, refrigerate at 4°C	6 months
	Magnesium	SM: 3120 B. Inductively Coupled Plasma (ICP) Method	ICP Spectrometer - Perkin Elmer Avio 200	0.03 mg/L	2% nitric acid, refrigerate at 4°C	6 months

Test Location	Test	Method	Equipment Description	Method Detection Level	Preservation Technique	Holding Time
	Iron	SM: 3120 B. Inductively Coupled Plasma (ICP) Method	ICP Spectrometer - Perkin Elmer Avio 200	0.01 mg/L	2% nitric acid, refrigerate at 4°C	6 months
	Chlorine (Free)	Hach Method 8021	HACH DR 2700 Spectrophotometer	0.02 mg/L as Cl_2	N/A	Analyze immediately
	DOC	SM: 5130 C. Persulfate-Ultraviolet or Heated-Persulfate Oxidation Method	Teledyne Tekmar Total Organic Carbon Fusion UV/Persulfate Analyzer	0.01 mg/L	2% phosphoric acid, refrigerate at 4°C	28 days
	TTHMs	SM: 6232 B. Gas Chromatograph	Agilent 6890N Network Gas Chromatograph	10 µg/L	Sodium sulfite, refrigerate at 4°C	14 days
	UV-254	SM: 5910 B. Ultraviolet Absorption Method	Realtech P300 UV254	0.01 cm^{-1}	N/A	48 hours
	Sulfate	SM: 4110 B. Ion Chromatography (IC); SM: 4500 B. Argentometric Method	IC - Dionex ICS-1100 with AS40 Automated Sampler	0.004 mg/l	Refrigerate at 4°C	28 days
	Bromide	SM: 4110 B. Ion Chromatography (IC); SM: 4500 B. Argentometric Method	IC - Dionex ICS-1100 with AS40 Automated Sampler	0.004 mg/l	Refrigerate at 4°C	28 days
Advanced Environmental Laboratories, Inc. (Altamonte Springs, FL)	HAA5	SM: 5710 D.	Agilent 6890N Network Gas Chromatograph	3 µg/L	Ammonium chloride, refrigerate at 4°C	14 days
	Bromate	EPA 300.1	IC Spectrometer	3.7 µg/L	EDA, refrigerate at 4°C	14 days
SGS Laboratories Inc. (Scott, Louisiana)	Formaldehyde	SW846 8315	GC/LC Semi-volatiles	2 µg/L	Refrigerate, 4°C	3 days

Test Location	Test	Method	Equipment Description	Method Detection Level	Preservation Technique	Holding Time
Calgon Carbon	Abrasion Number	TM-9	N/A	N/A	N/A	28 days
	Apparent Density	TM-7	Oven	N/A	N/A	28 days
	Iodine Number	TM-5 ASTM D2866	Titration	N/A	N/A	28 days
	Particle Distribution	TM-4	Mass	N/A	N/A	28 days

Table 4-2: Methods to Zeroing and Calibration of Instrumentation

Analyte	Method of Calibration or Zeroing
Chlorine, Free	Zero by filling the sample cell with solution, place cell in the unit and press zero.
Dissolved Oxygen	Calibrate by placing the galvanic probe into a holder with a wetted sponge for 10 minutes, then press calibrate.
Dissolved Ozone	Zero by creating a blank. Fill a 150 mL breaker with DI water and break open an ampul in the water, place in the unit and press zero.
ORP	Calibrate by placing the sensor into calibration solution at a specific level of mV and pressing zero.
pH	Calibrate by placing the pH sensor into standardized solutions at pH's of 4, 7 and 10 and pressing calibrate on the unit with the sensor in each solution.
Temperature	Calibrate against a certified thermometer.
Turbidity	Calibrate using samples containing standardized NTUs.
Total Sulfide	Zero by creating a blank. Place 10 mL of DI water into a cell and mix 0.5 mL of Sulfide reagent 1 and Sulfide reagent 2 into the solution by slowly inverting the cell after inclusion of the reagents. Let the solution stand for 5 minutes, insert the cell into the unit and press zero.
UV_{254}	Zero by pouring DI water into a cell, placing the cell into the unit, and pressing zero.

DBP Formation Experimentation

During DBP formation experimentation, samples were analyzed for their respective chlorine residual, pH, temperature and DBP formation after their extended period of simulated incubation. Groundwater from the raw influent line was also aerated and underwent DBP formation experimentation as a control for either studies. Prior to DBP analysis, groundwater samples were aerated overnight to removed volatile compounds that may interfere with the proceeding experiment. To quantify the required chlorine dosage for each sample to achieve a residual between 0.2 mg/l Cl_2 – 1.0 mg/L Cl_2 after 48-hours at an incubation at 30°C, each sample was initially dosed with three separate chlorine doses and the sample with the lowest residual within the set range was chosen. After determining the required chlorine doses, 1000-mL of sample for each condition was dosed with chlorine with a stock solution with a strength of approximately 38,000 mg/l Cl_2 was then mixed on a stir-plate with a stir bar for approximately 45-seconds. Stock strength of the chlorine solution was measured prior to each experimentation event. After mixing for the allotted time, samples were measured for their zero hour chlorine residual, poured into 60 mL amber bottles, and incubated at 30°C for 24- hours and 48-hours. This methodology sought to replicate the worst-case conditions influencing water in a distribution system, which maximizes the potential for DBP formation. After the predetermined incubation times has expired, samples were removed from the incubator and chlorine residuals of each sample were measured. Samples collected for TTHM analysis were then quenched with sodium sulfite and stored in a refrigerator at 4°C for up to two weeks prior to gas chromatography analysis. Samples collected for HAA5 analysis were poured into 200-mL amber vials provided by American Environmental Laboratories, Inc. (AEL) (Altamonte Springs, FL), quenched with ammonium chloride and stored in a refrigerator at 4°C for up to two weeks prior to their analysis. The employed simulation of a potable water system is conceptual in nature and is intended as a use to provide for analytical estimations

of DBP formation within a full-scale PWS. As to avoid the loss of volatile compounds during the experimentation of DBP FPs, samples were prevented from being over-exposed to the atmosphere and light.

Organic Composition Determination

NOM acts as the major natural DBP precursor for the formation of DBPs in the UCF water supply. To better understand the reduction of NOM post-ozonation and GAC filtration, samples taken from each port of the pilot were measured for UV_{254} absorbance and DOC concentration, and SUVA was calculated after knowledge of either constituent was discovered. Additionally, raw and ozonated samples were also studied for their fluorometric behavior. Upon arrival to the UCF Water Quality Laboratories, NOM samples were refrigerated at 4°C until the required analysis began. Prior to their analysis, NOM samples were filtered through 0.45-micron filters using a vacuum filter. Filtered samples for DOC quantification were then poured into 60 mL amber vials, acidified with 800 µl of phosphoric acid and stored for up to two weeks in a refrigerator at 4°C before being ran on a Teledyne Tekmar Total Organic Carbon Fusion machine. For all other filtered NOM samples, sampling bottles were reprimed with the filtered sample and the filtered sample was poured back into their respective sampling bottles and stored in a refrigerator at 4°C for up to a week before initial analysis was completed.

Affiliated techniques to produce the required NOM fraction results were completed using the methods presented in Table 4-1. SUVA was then calculated through Equation 2.2 from Chapter 2, which is derived using the resulting DOC and UV_{254} values. Analysis for fluorometric behavior was completed with emission and excitation bandwidths set to 1 nm and excitation wavelengths ranged from 250 nm to 600 nm and emission wavelengths ranged from 280 nm to 520 nm.

Pilot System Process

Facilitation of the following treatment studies were completed through installation of a pilot at the UCF WTP with the capabilities of advanced oxidation through ozone and GAC filtration. The system diagram for the integrated ozone-GAC pilot at the UCF WTP can be observed in Figure 4-1 and pictures of the ATS-15 Guardian ozone generator and two GAC pilot columns also at the UCF WTP are included in Figure 4-2. Raw groundwater from the UCF GST influent line was supplied to the pilot through the top of the ozone skid's contact tank using pressure driven by head generated by the GST. Upon entering the contact tank, water was continuously removed through the bottom of the vessel into a pressurized loop containing the point of ozone injection. At the point of ozone injection, a decrease in pipe diameter forced water to generate a vacuum through the venturi effect which would mix the gas into an aqueous mixture, and the resulting solution would be recirculated back into the bottom of the contact tank. For the integrated ozone-GAC study, the pilot was operated with an applied dose of 7.2 mg/l O_3, which resulted in a residual of 0.30 mg/l O_3 in the contact tank after demand of the raw water was satisfied. Ozonated water in the recirculation loop was also bypassed into a separate line which either directed the flow into one of two GAC pilot columns or into a grate for disposal. Flow was wasted to maintain steady state conditions in the ozone skid contact tank, which would overheat and irritate solubility of ozone if too little flow exited the ozonation process. Flows directed through the GAC columns were monitored using flow totalizers, which were controlled using flow meters containing a range of control from 0.01 gallons per minute (gpm) to 1 gpm and effluent from the GAC columns were disposed.

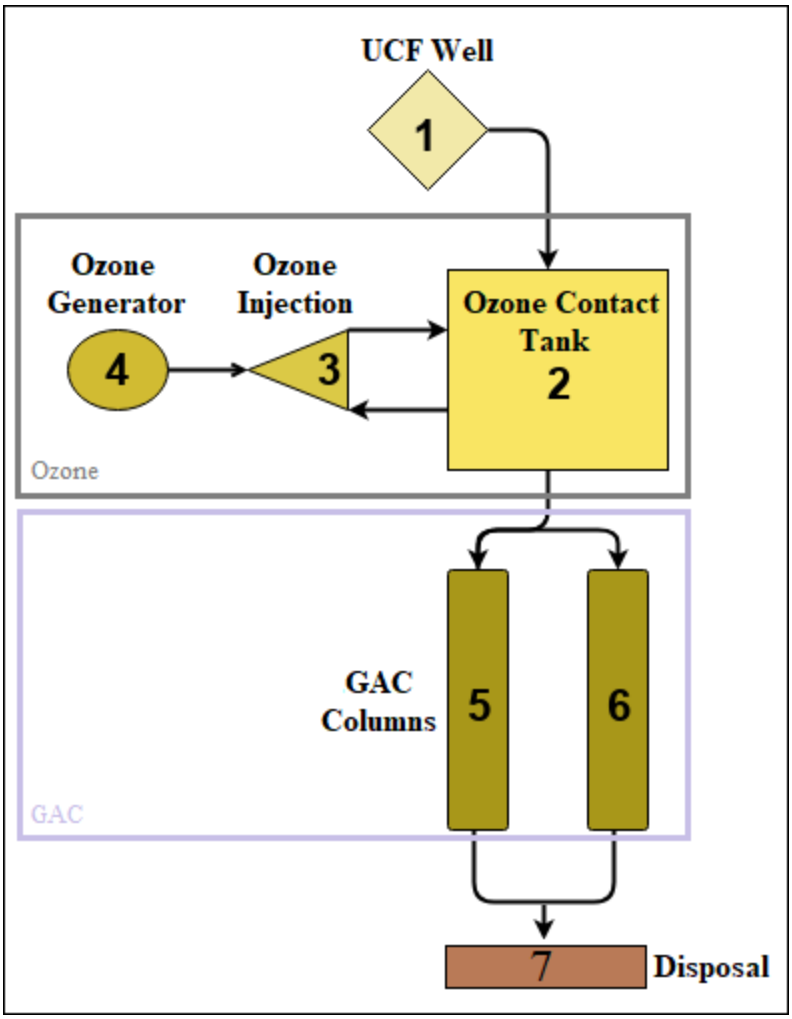

Figure 4-1. Process Schematic for the Integrated Ozone-GAC Pilot

(a) (b)

Figure 4-2: a) View of the Integrated Ozone and GAC Pilot, b) GAC Pilot Carbon Columns

Operation of the integrated ozone-GAC pilot would be prevented if certain conditions were meet during facilitation of treatment. Such errors that were encountered during operation of the pilot equipment were mainly due to operational constraints arisen from a low demand incurred by the UCF PWS, which would often prevent the well pumps from operating as the GST would remain full for extended periods of time. During these periods, the pilot would rely on pressure driven by the GST's influent line to supply water to system processes. This pressure would often dwindle after sustained use and loss of water to the ozone skid would cause the ozone generator to shut off prematurely, preventing operation of the pilot. Additional issues that would cause for the pilot to shut off prematurely, not associated with low flow events, were due to mechanical errors associated with low oxygen purity and variable injection pressure. Such errors became an issue as operators were unable to monitor the pilot for all hours of the day, preventing staff from maintaining routine scheduling of pilot operation.

Ozone Generator Equipment

The ozone generator used in this study was a Guardian Manufacturing ATS-15 (ozone skid), which houses the capability to dose ozone up to 11 mg/l O_3 at the designed flow rate of 15 gpm (Guardian Manufacturing, 2021). Production of ozone was completed through use of an oxygen enrichment system, which converted ambient air into highly concentrated oxygen through a process called Pressure Swing Adsorption (PSA). PSA processes generate oxygen enriched gases by stripping nitrogen from ambient air through filtration by pressurized cylinders containing a mixture of thermally modified zeolite and diatomaceous earth, producing oxygen at a purity of approximately 96%. The ozone skid would then direct the oxygen enriched gas into a Plasma Technics 50 g Plasma Block ® (Plasma Block), which used the corona discharge method to generate ozone at 5-10% weight (Plasma Technics, 2021). Most of the generated ozone, and a small amount of oxygen

resulting from its decomposition, were then diffused into the injection point with the flow of groundwater and an aqueous mixture of ozonated water was created. Undissolved gases would float to the top of the tank and exit through the off-gas destruct unit located at the top of the ozone skid where gaseous ozone was converted back into oxygen. Design of the off-gas unit was included to comply with the United States Department of Labor Occupational Safety and Health Administration (OSHA), who constituted that an employee must not be exposed to ozone above its permissible exposure limit over an eight hour time-weighted average value of 0.1 parts per million (ppm) (OSHA, 2006).

Monitoring equipment onboard the ozone skid could measure the ozone residual and water level in the contact tank, ozone concentration in the ambient air and the ozone generator's voltage, amperage, and total runtime. Such values monitored by the ozone skid were reported every five-seconds and saved onto its onboard memory storage. Calibration of the ozone skid's set ozone residual level and scheduling of the pilot were both controlled though use of the skid's programmable logic controller (PLC) which provided a user interface via a touchscreen mounted on the ozone skid. Through the PLC, the pilot was programmed to turn on and begin dosing the influent flow to a residual of 0.3 mg/l O_3 in the morning at 9:30 AM and off in the evening. To determine the applied ozone dose performed by the ozone skid during the integrated ozone-GAC study, operational parameters such as the UCF groundwater iron and sulfide concentrations, generator current and amperage, oxygen flow, liquid flow and ozone residual in the contact tank of the ozone skid were logged over the duration of the study. The calculation of ozone dosage was also be estimated through combination of the ozone residual concentration and stoichiometric chemical demand equations for sulfide and iron, which are included in Equation 2.10 and Equation 2.11.

Activated Carbon Pilot Columns

Operation of the integrated ozone-GAC pilot to treat the ozonated flow was completed through use of two GAC pilot columns, either containing the following Calgon series of carbons: FS-400 and HPC-830. Effectiveness of pilot column operation was determined through the monitoring and analysis for DBP precursor reduction and formation of DBPs from the column effluent. Both carbon types were manufactured by Calgon and the virgin carbon characteristics of either carbon type can be observed in Table 4-3.

Table 4-3: Virgin Carbon Characteristics

Carbon Type	Iodine Number (mg/g)	Abrasion Number	Apparent Density (g/cc)	Effective Granule Size (mm)
HPC-830	1000, min	80	0.27, min 0.37, max	0.60 – 2.4
FS-400	1000, min	75	0.44	0.43 – 1.7

The HPC series of carbon is produced by Calgon Caron, and contain carbon types that are low-density, kosher, coal-based which can be reactivated after exhaustion (Calgon Carbon, 2015). HPC-830 virgin carbon is also characterized by its low apparent density of 0.37 g/cc^3 to 0.43 g/cc^3, which gives the carbon the advantage of being a low cost per unit volume alternative to denser carbon options. The HPC-830 carbon type also benefits from a reduced contact time due to its large volume of transport pores.

The Filtrasorb series is also manufactured by Calgon Carbon and is produced from the re-agglomeration of bituminous coal for the purpose of removing organic substances from water (Calgon, 2015). The FS-400 carbon type has a high mechanical strength due to re-agglomeration, attributing to its hardness and apparent density of 75 g/cc^3 and 0.54 g/cc^3, respectively, at virgin

conditions. The carbon's high mechanical strength should allow for a sustained and effective operation through multiple backwashes without the production of additional fines as the carbon ages. FS-400 carbon is also re-activated, which produces small and large pore sizes to allow for a broad range of adsorption of low and high molecular weight organic compounds (Calgon, 2015). FS-400's apparent density also increases its adsorptive capacity at the disadvantage of an increase in O&M costs since the cost per volume will be higher as compared to a carbon with a lower density. Neat (stock) FS-400 carbon contains particles with diameters that range between 0.43 mm and 1.7 mm, while virgin HPC-830 carbon contains particles with diameters that range between 0.60 mm and 2.4 mm. Both carbon types also possess a fines content of approximately five-percent.

The pilot columns were designed to uphold a predetermined flow of 0.15 gpm at its designed dimensions, producing an EBCT of 3.5 minutes within either column. Flow for the GAC columns was controlled using two Blue White F-550 adjustable flowmeters and total flow was measured using two FlowIQ ® 2100 totalizers.

Packing of the GAC pilot columns was completed at the UCF Laboratories. To prevent excess carbon from escaping the pilot columns, a six-inch layer of coarse aquarium gravel was first poured into the bottoms of both pilot columns. Additionally, before entering either pilot column, the coarse aquarium was washed with distilled (DI) water. An 18-inch layer of GAC, one column receiving FS-400 and the other HPC-830, was then poured into either column on top of the coarse aquarium gravel. The packed columns were then backwashed with DI water until a bed expansion of 30% was achieved and observable fines were undetected in the effluent. After backwashing, the carbon columns were installed onto the wall of the UCF WTP pump room and allowed to soak for a week before the pilot was first operational.

Laboratory Quality and Control

Laboratory and field quality control measures were employed during both studies presented in this thesis to ensure proper quality assurance and quality control (QAQC) were followed. Duplicates of field measurements were taken during the analysis for pH, temperature, conductivity, turbidity, ozone residual, dissolved oxygen, oxidation reduction potential and total sulfide. Laboratory analysis completed at UCF Laboratories, AEL, SGS and Calgon Corporation followed the procedures in accordance with EPA and the *Standards and Methods for the Examination of Water & Wastewater* (Baird et al., 2017). Each laboratory follows a Laboratory Quality Assurance Plan, which requires quality control to be monitored and reported for each method used (EPA, 2005). Laboratory analyses for TTHMs included duplicates and spikes for every fifth sample to ensure precision and accuracy. Calculation of QAQC can be observed in Equations 4.1 – 4.5, and the control level (CL) and warning levels (WL) for the associated parameters were calculated using the first ten samples analyzed in adherence with *Standards and Methods for the Examination of Water & Wastewater* (Baird et al., 2017). For DOC and UV_{254} measurement, replicates and duplicates were analyzed from the raw well line and spikes were completed for DOC analysis every five samples.

$$RPD = \frac{\frac{|Sample\ Result - Duplicate\ Result|}{Sample\ Result + Duplicate\ Result}}{2} * 100 \tag{4.1}$$

$$Percent\ Recovery = \frac{Quantity\ Measured}{Quantity\ Added} * 100 \tag{4.2}$$

$$R^o = d_2 s \tag{4.3}$$

$$CL = R^o \pm 3s * R = D_4 R^o \tag{4.4}$$

$$WL = R^o \pm 2sR = R^o \pm \frac{2}{3}(D_4 R^o - R^o) \tag{4.5}$$

Where, RPD is the relative percent difference, R^o is the mean range, s is the standard deviation, d_2 is the factor of to convert standard deviation to mean range, equal to 1.128 for duplicates, CL is the control level, WL is the warning level, R is the range and D_4 is the conversion factor to convert mean range to CL, equal to 3.267 for duplicates.

CHAPTER 5. RESULTS AND DISCUSSION

The results presented in this chapter were reported from analytical observations for NOM and DBP formation performed on both the stand-alone ozone oxidation studies in addition to the integrated ozone-GAC filtration pilot located at the UCF WTP. Water quality monitoring for the specific parameters profiling the treatment processes evaluated were evaluated to determine the treatment effectiveness of both the stand-alone ozone and integrated ozone-GAC processes.

For the stand-alone ozonation component of the study, the effectiveness for each ozone dose to reduce the NOM originating from the UCF groundwater was measured through DOC, UV_{254} and spectrofluorometry. Observed TTHM and HAA5 formation results were analyzed to determine the effective reduction in TTHM and HAA formation post-ozone oxidation and bleach disinfection.

For the integrated ozone-GAC process study, DOC, UV_{254} and SUVA were first used to determine the NOM fractionation remaining in the processed water. Each GAC column was assessed for DOC and UV_{254} breakthrough in terms of EBVs for each GAC column. DBP formations were compared with NOM results to estimate the TTHM exhaustion for both pilot column carbon types.

Stand-Alone Ozone Oxidation Performance

Over a four-week period from January 27, 2021 to February 24, 2021, the UCF groundwater was exposed to varying levels of ozonation through use of the ozone generator section of the integrated ozone-GAC pilot located at the UCF WTP. The stand-alone ozone dose studies were conducted in duplicate and expressed as trial one (T1) and trial two (T2). Results associated with the stand-alone ozonation study included the reaction of NOM through DOC and UV_{254} monitoring, behavior of fluorimetry and reduction of DBPs, mainly TTHMS, after application of a range of ozone doses on the raw UCF groundwater.

Water Quality Results

The selected ozone dosage quantities targeted for this study are recorded with the residual after the ozone demand for the generator was satisfied at the time of experimentation. The contact tank was flushed for a period of 30 minutes after changing the generator's residual setting before a subsequent test run was performed and a water sample was collected for ozone decay. The residuals tested in this study were 0.30 mg/l O_3, 0.80 mg/l O_3, 1.5 mg/l O_3, 3.0 mg/l O_3 and 6.0 mg/L O_3, each marked respectively in the results as ozone residual #1, #2, #3, #4 and #5. Through each experimented dose, the concentration of ozone in the contact tank was variable and was not sustained exactly at the inputted dose of ozone. The lowest ozone residual setting was set to 0.3 mg/l O_3 (with an applied dose of 7.2 mg/l O_3) since the ozone generator could not produce an ozone residual below zero. It is also to be noted that when the ozone generator was adjusted to provide the highest residual of 6.00 mg/L O_3, the skid's ozone generation unit was at full capacity. The highest actual measured residual observed within the contact tank was in dose #5 which

registered 4.00 mg/L O_3; however, the concentration was variable through the experiment. The resulting water quality and NOM results from the study are included in Table 5-1.

Table 5-1: Water Quality Results from the Stand-alone Ozonation Study for Trials 1 and 2

Parameter	Raw		#1		#2		#3		#4		#5	
	T1	T2	T1	T2	T1	T2	T1	T2	T1	T2	T1	T2
Residual Setting (mg/L O_3)	N/a	N/a	0.3	0.3	0.8	0.8	1.5	1.5	3.0	3.0	6.0	6.0
pH	7.41	7.49	7.41	7.58	7.78	7.49	7.75	7.41	7.69	7.50	7.68	7.49
Temperature (°C)	26.4	23.9	27.4	26.8	24.5	27.3	24.9	25.8	21.6	27.5	27.2	26.4
Actual Ozone Residual (ATS-15) (mg/L)	-[2]	-[2]	0.30	0.31	0.78	0.88	1.44	1.74	2.96	2.90	3.73	3.70
Actual Ozone Residual (HACH) (mg/L)	-[2]	-[2]	0.44	0.37	1.06	0.88	-[*]	-[*]	-[*]	-[*]	-[*]	-[*]
ORP (mV)	-167	-122	241	309	550	565	657	574	729	761	845	831
UV_{254} (cm^{-1})	0.0840	0.0811	0.0329	0.0350	0.0318	0.0320	0.0262	0.0289	0.0224	0.0212	0.0181	0.0199
DOC (mg/L)	2.45	2.40	2.32	2.33	2.28	2.37	2.24	2.26	2.13	2.09	1.96	2.03
SUVA (L/mg/m)	3.43	3.38	1.42	1.50	1.39	1.35	1.17	1.28	1.05	1.01	0.92	0.98
Formaldehyde (ppb)[3]	-	-	36.1	-	-	-	43.3	-	-	-	-	-
Bromate (ppb)[3]	-	-	< 3.7	-	-	-	< 3.7	-	-	-	-	-

[*]: *The MDL of the HACH DR 2800 prevented its measurement of ozone residuals on samples above 1.50 mg/l O_3.*

[2]: *Dissolved ozone residual measurements were not taken on the raw groundwater samples.*

[3]: *Formaldehyde and bromate were collected during the first trial for doses #1 and #3.*

Reported in Table 5-1 are results for the dissolved ozone concentration of ozonated samples as monitored by a HACH DR2800 in triplicate, with an acceptable range of 0.1 mg/l O_3 to 1.5 mg/l O_3 residual, and the monitored dissolved ozone residual concentrations as reported by the ozone generator's monitoring equipment. The highest achievable residual for the set of samples was approximately 3.7 mg/l O_3; however, the dose of ozone applied to the influent varied throughout each trial. For a higher ozone residual to have been achieved, the alteration of operational conditions to improve the solubility of ozone in the contact tank would have been required. Temperature and pH within the contact tank of the ozone generator varied by day depending on the groundwater quality and length of ozone generator operation. The results for pH and temperature were unaffected by oxidation and the resulting ORP measurements increased from 275 to 840 mV. Additionally, sampling for formaldehyde and bromate was completed during the first trial for doses #1 and #3.

DBP Precursor Results

At the time of ozone dosing, impact on NOM fractioning in the effluent from the ozone generator was monitored. This was completed through the determination of the DOC, UV_{254} and SUVA of raw and ozonated samples. Additionally, fluorescence of the raw and some ozonated samples were analyzed through the procreation of EEMs. As a result, relationships between the monitored DOC and UV_{254} of the set of ozonated samples were observed. The correlation between results for DOC and UV_{254} from the ozonated samples are included in Figure 5-1.

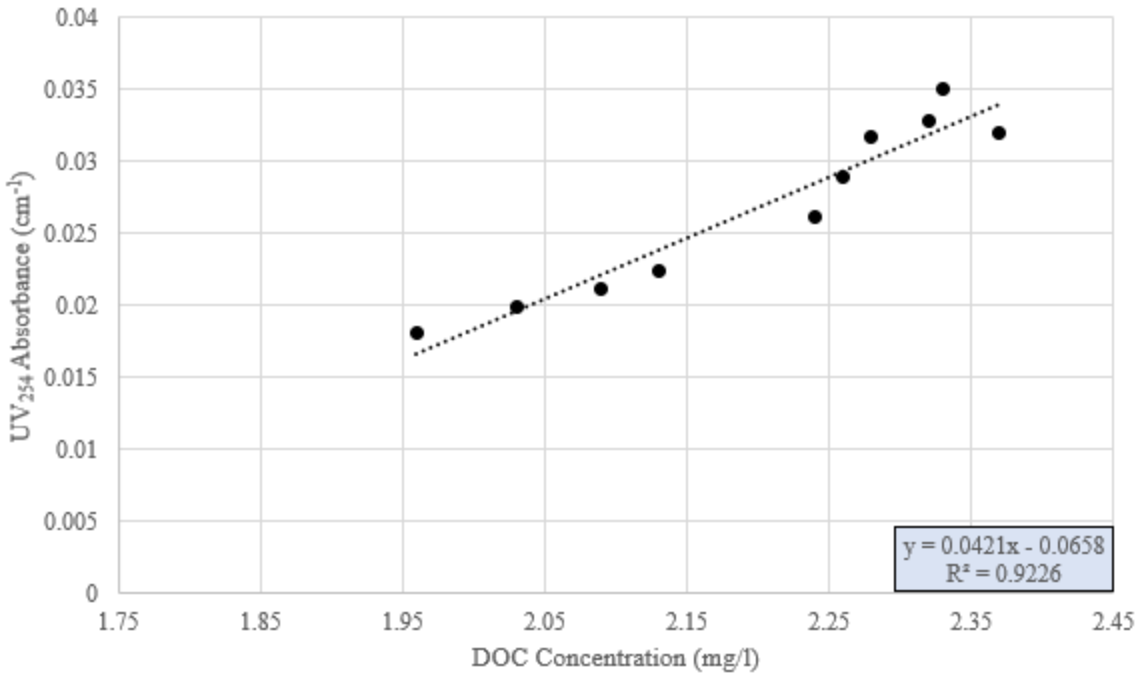

Figure 5-1: Correlation between DOC and UV_{254} for the Stand-alone Ozonation Study

The reported r-squared value of Figure 5-1 was 0.9226, which displays a positive relationship between the DOC and UV_{254} results from the stand-alone ozonation study. Further observations on the impact of DOC and UV_{254} by the stand-alone ozonation process, in comparison to the DOC and UV_{254} results from the groundwater influent line presented in Table 5-1, are included in Figure 5-2.

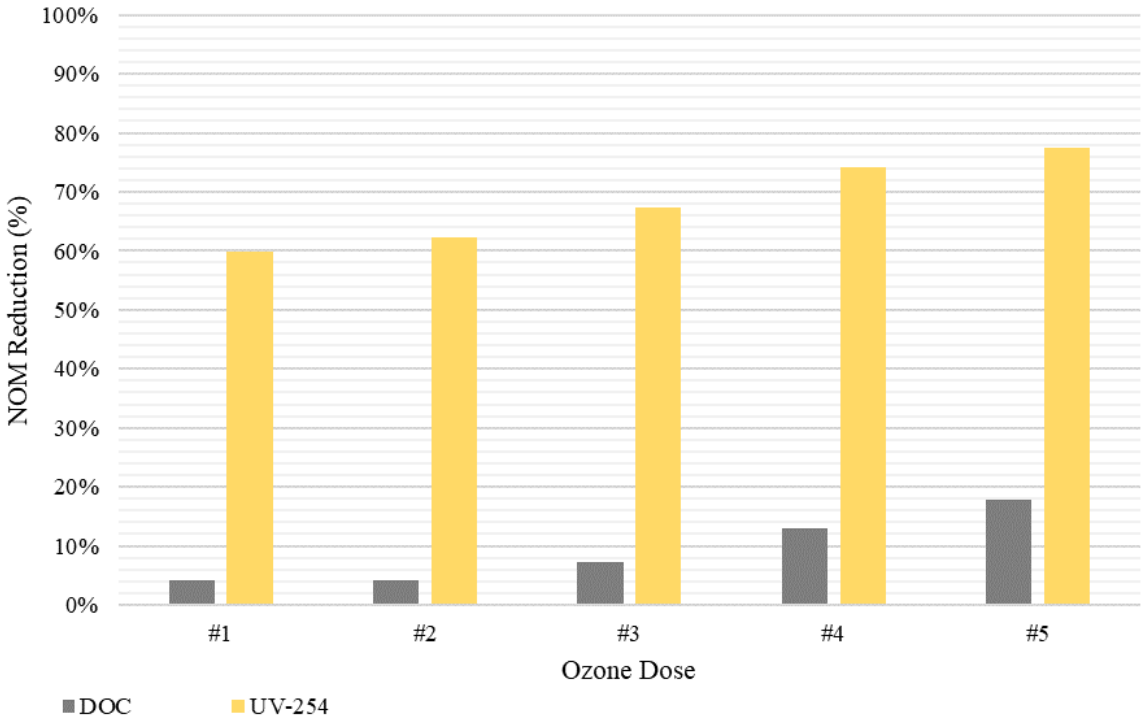

Figure 5-2: Average DOC and UV_{254} Reduction by the Stand-alone Ozonation Study

A relationship between the applied dose of ozone and NOM impaction was observed during the stand-alone ozonation study, where an increase to the applied ozone dose resulted in a decrease in the levels of UV_{254} and DOC concentration in the effluent flow of the ozone generator. UV_{254} was reduced far greater than DOC by the applied ozone, further exemplifying that the ozonation process was more efficient at degrading the aromatic, UV absorbent fraction of NOM in the UCF groundwater supply. This resulted in the measured DOC and UV_{254} of the ozonated samples being reduced by up to approximately 80% and 20%, respectively. As the ozone dose was increased, the efficiency of UV_{254} and DOC reduction also increased by 18% and 14%, respectively. This would suggest that the lowest dose of applied ozone, which was sufficient meeting the ozone demand of the raw groundwater and providing for a low ozone residual, was sufficient to reduce over half of the UV absorbent fraction of NOM and a small portion of the DOC portion of NOM in the UCF

groundwater. The observed reduction of NOM in each ozone dose would suggest the resulting formations of DBPs would also be minimized, however the difference in reduction between the lowest and highest doses of ozone should be minimal. Table 5-1 further displays this relationship, where the raw groundwater sample contained a mix of humic and non-hmuc organics and the ozonated samples were observed to contain non-humic organics. Further determination on the alteration of NOM through the ozonation of groundwater can also be observed in the change to the fluorometric behavior of samples through fluorometric EEMs, which are displayed in Figure 5-3, Figure 5-4, and Figure 5-5.

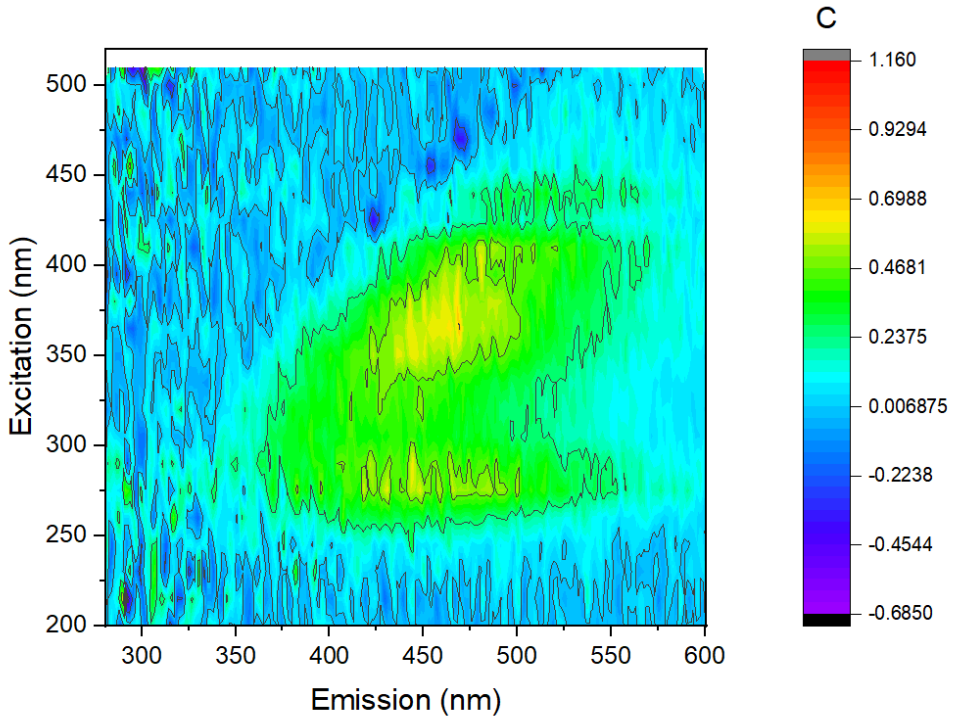

Figure 5-3: EEM of the Raw UCF Groundwater Supply

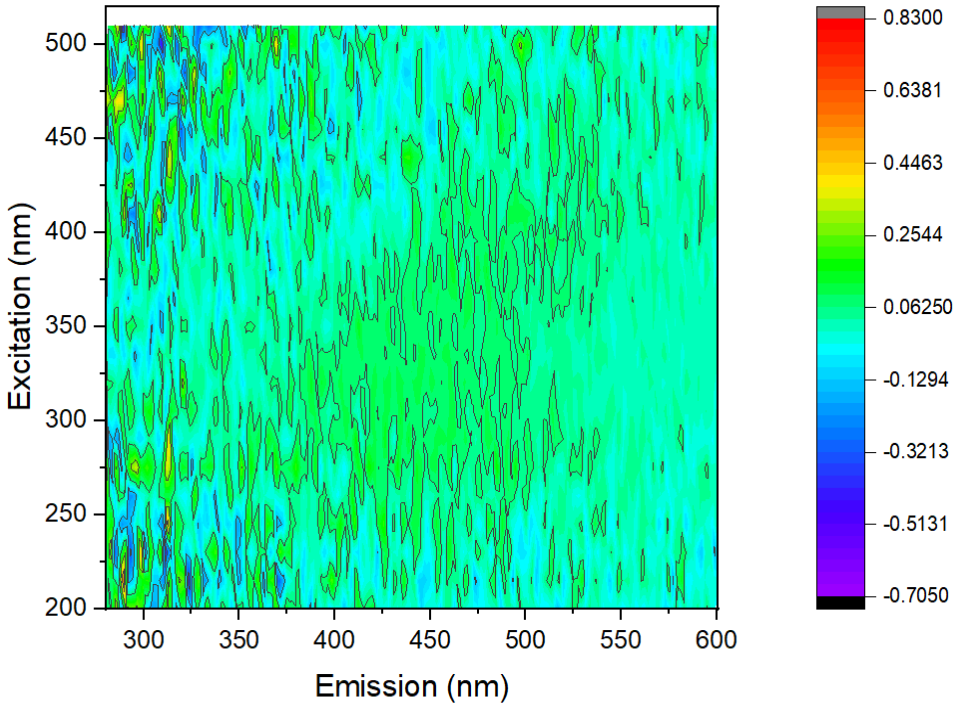

Figure 5-4: EEM of the UCF Groundwater Supply Ozonated to 0.3 mg/l O_3 Residual

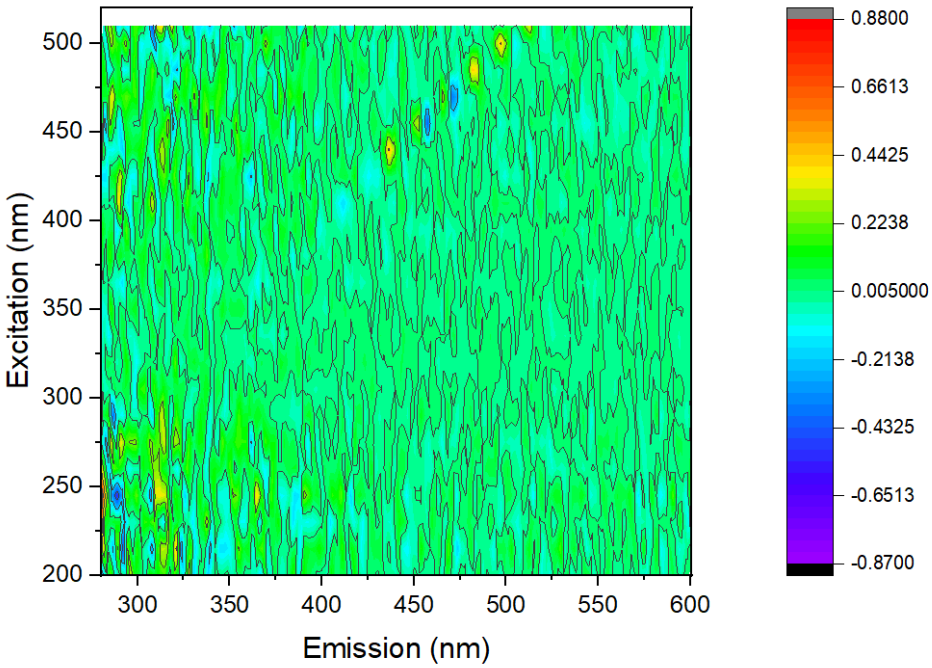

Figure 5-5: EEM of the UCF Groundwater Supply Ozonated to 3.7 mg/l O_3 Residual

Figure 5-3 displays a large presence of fluorescent organic media within the humic region of the resulting EEM. Initial ozonation of the UCF groundwater with the lowest dose had a large impact on the fractionation of NOM, resulting in a low amount of visible fluorescence within the humic region of the EEM. Further ozonation of the UCF groundwater with the highest dose completely removed visible fluorescence.

DBP Formation Results

The reduction in chlorine residuals resulting from DBP formation experimentation, at an average between the two trials, are included in Table 5-2. Also included in APPENDIX A are the water quality results for free chlorine, pH, temperature, and turbidity of samples as monitored and collected during the stand-alone ozonation DBP formation experimentation.

Table 5-2: Chlorine Residual Reduction of DBP Samples from the Stand-alone Ozonation Study

Sample	Dose (mg/l Cl_2)	0-hr Residual (mg/l Cl_2	Initial % CL_2 Reduction	24-hr Residual (mg/l Cl_2)	% CL_2 Reduction at 24-hr	48-hr Residual (mg/l Cl_2)	% CL_2 Reduction at 48-hr
D1	5.0	2.6	46%	0.92	82%	0.66	87%
D2	5.0	2.9	42%	1.1	80%	0.71	86%
D3	5.0	3.0	42%	1.2	77%	0.81	85%
D4	5.0	2.9	38%	1.3	74%	0.98	81%
D5	5.0	2.8	42%	1.3	72%	0.97	79%

As the applied dose of ozone was increased, the required dose of chlorine to supplement a residual between 0.2 mg/l Cl_2 and 1.5 mg/l Cl_2 after 48-hours of incubation was unaffected, however the efficiency of samples to maintain said chlorine residual was increased. During both trials, each sample required a dose of 5.0 mg/l Cl_2 and the resulting reduction in chlorine residual, as compared between the lowest and highest doses of ozone, was mitigated by 10% and 12% at 24-hours and 48-hours of incubation. This would suggest that application of an ozonation process to the UCF groundwater would increase the effectiveness of the UCF PWS to maintain its residual of chlorine at prolonged holding times. The average resulting formation of TTHMs at 24-hours and 48-hours are included in Figure 5-6 and the tabulated TTHM results for the ozonated samples with percent reduction of DBP formation, as compared to results from the aerated groundwater samples, are displayed in Table 5-3. Such reductions in TTHM formation by the stand-alone ozonation process were calculated using the averaged formation potential results analyzed from the raw groundwater influent line in mid-January 2021. Individual water quality and DBP results observed during formation experimentation of the UCF groundwater is included in APPENDIX A.

Table 5-3: TTHM Formation and Percent Reduction by the Stand-alone Ozonation Study

Trial No.	Sample	24-hr TTHM FP	24-hr TTHM % Reduction[1]	48-hr TTHM FP	48-hr TTHM % Reduction[1]
Trial 1	#1	81.3	1.57	97.0	-2.63
	#2	76.6	7.26	92.7	1.92
	#3	71.2	13.8	89.1	5.73
	#4	69.4	16.0	86.3	8.69
	#5	65.0	21.3	83.0	12.2
Trial 2	#1	78.4	2.08	97.3	-2.95
	#2	77.0	6.78	94.3	0.22
	#3	71.6	13.3	87.9	7.00
	#4	67.0	18.9	86.8	8.16
	#5	64.5	21.9	78.4	17.1

[1]: *Percent reduction is calculated with the average groundwater TTHM FP from mid-January 2021.*

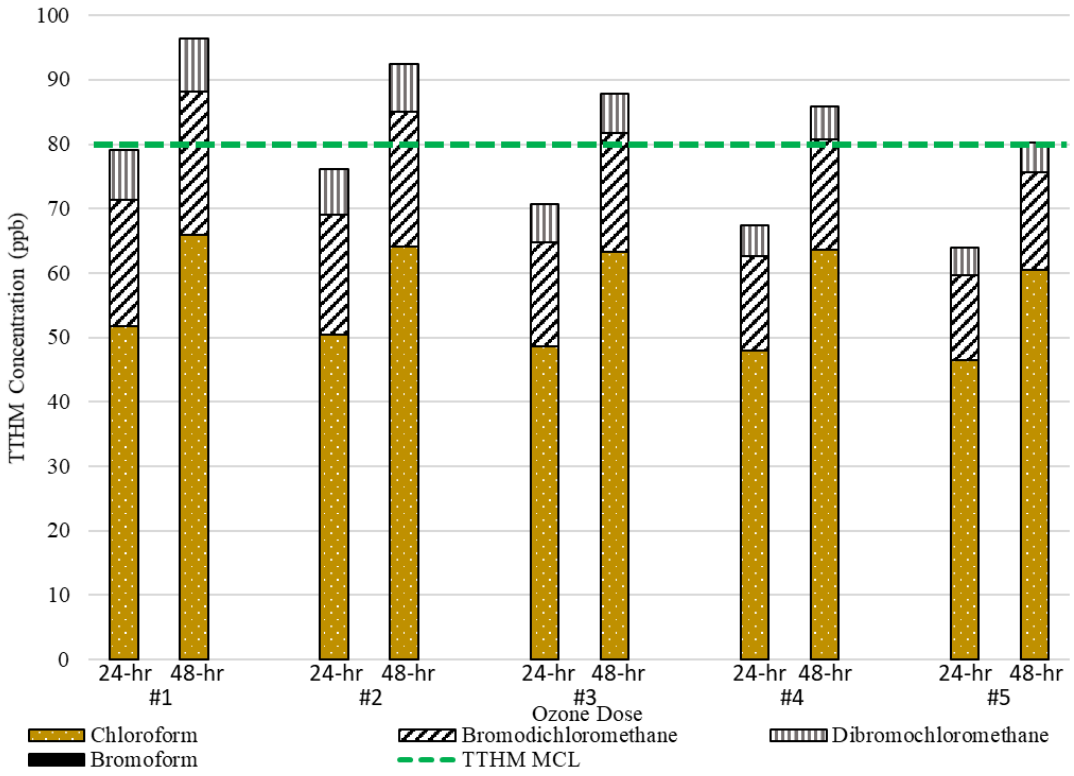

Figure 5-6: Average TTHM Formation at 24 and 48-hours for the Stand-alone Ozonation Study

TTHM results from the stand-alone ozonation study would suggest that an increased dose of ozone would reduce the formation of TTHMs in the UCF distribution system. This relationship of decreased TTHM concentrations at increased ozone dosages was observed between both trials, where on average the 24-hour set decreased from 80 ppb to 65 ppb and the 48-hour set decreased from 97 ppb to 83 ppb. Additionally, the resulting TTHM formation for the sample containing the highest dose of ozone applied at 24-hours and 48-hours of incubation remained below and above the MCL, respectively. This would suggest that an applied ozone dose above 11 mg/l O_3 would be required to sufficiently reduce the amount of TTHMs to a level that would be deemed safe for public health. The UCF PWS has also been previously characterized with water ages above 48-hours of incubation, so TTHM formations at the highest dose of ozone would most likely exceed the MCL for the contaminant under real-world circumstances. Additionally, increases to the applied dose of ozone had very little impact on the speciation of THMs, as shown in Figure 5-7.

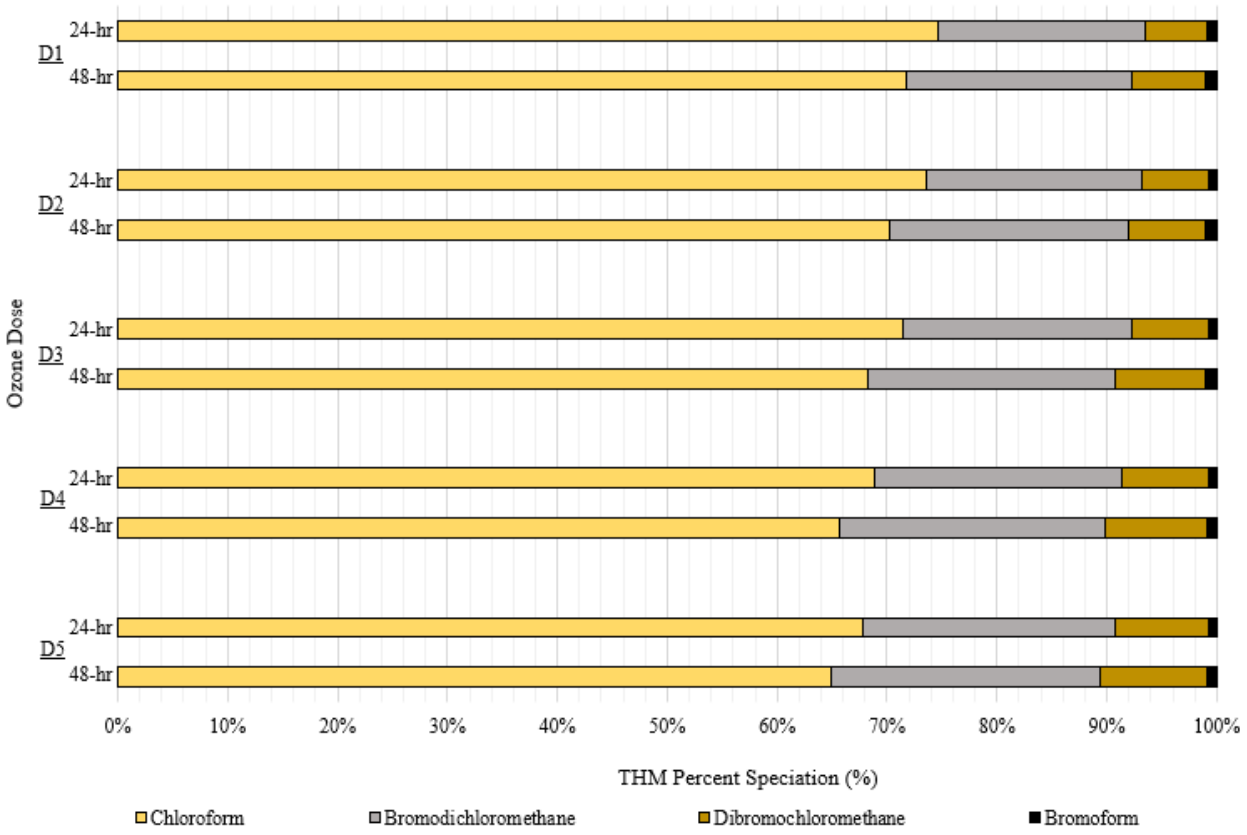

Figure 5-7: THM Speciation for the Stand-alone Ozonation Study

Increases to the applied dose of ozone to the UCF groundwater decreased the formation of chloroform and increased the formation of brominated DBPs. As the dose of applied ozone was increased, the percent formation of chloroform was also increased by 7% and the percent formation of BDCM and DBCM were decreased by 4% and 3%, respectively. However, it is to be noted that every measurement for bromoform was observed to be below the MDL for the instrument at a concentration of > 0.7 ppb, so further observations on the reduction of the compound could not be concluded on. Speciation results would suggest that the required ozone dose to effectively reduce THMs below the MCL would result in a high percent speciation of brominated DBPs, which would increase the hazards towards public health from the consumption of potentially carcinogenic, brominated DBPs. Additional results for HAA5 formations at 48-hours of incubation for four of

the five ozone doses trialed from the first round of ozonation experimentation are included in Figure 5-8.

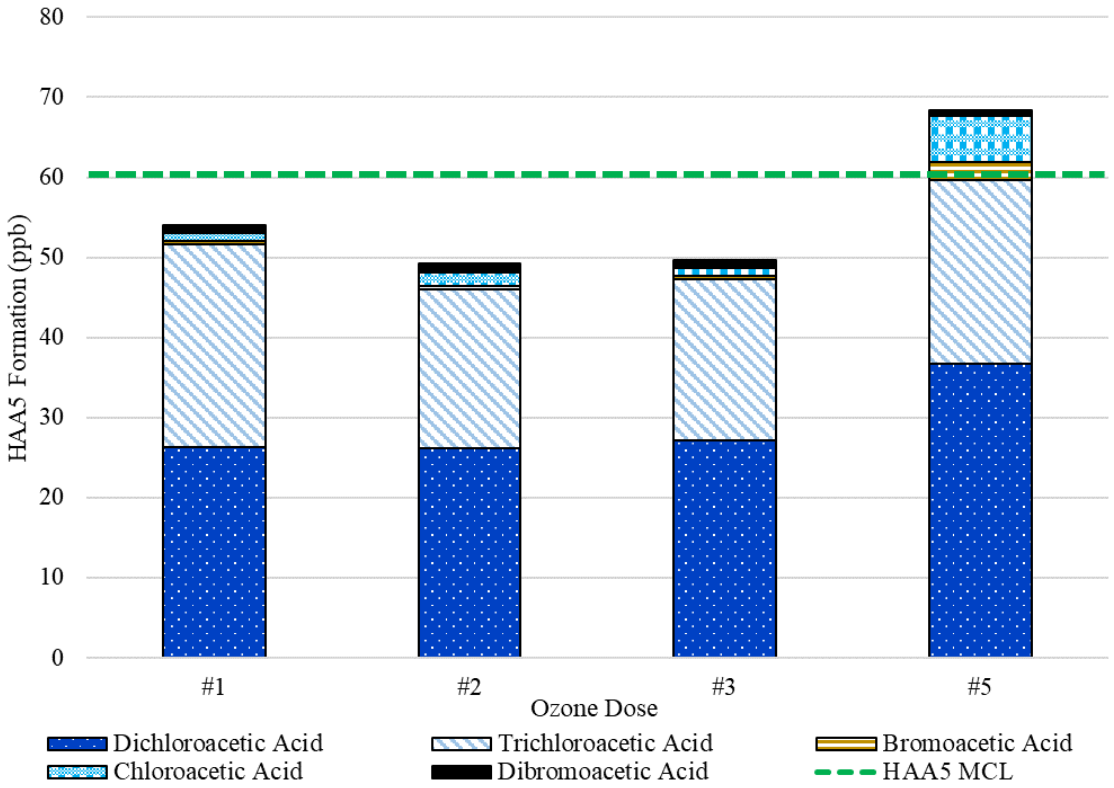

Figure 5-8: HAA5 Formation at 48-hours from the Stand-alone Ozonation Study

HAA5 formation results would suggest that the lower doses of ozone decreased the formation of HAA5s while the highest dose of ozone increased the formation for HAA5s. The observed increase in HAA5 formation for the highest dose of ozone resulted in an HAA5 concentration which surpassed the MCL of 60 ppb. As such, the installation of a stand-alone ozonation process by the Utility operating at an ozone dose equaling or exceeding the highest dose trialed may elevate HAA5 formations in the UCF distribution system beyond the threshold of the MCL, thus requiring further remediation.

Integrated Ozone and GAC Process Performance

The integrated ozone-GAC study was operated for a total of 420 hours and approximately 7000 EBVs over a period of three-months (November 21, 2020 - February 26, 2021). The observed average daily operating ozone residual and daily runtime of the pilot as reported by the Guardian ATS-15 ozone generator's monitoring equipment are included in Figure 5-9.

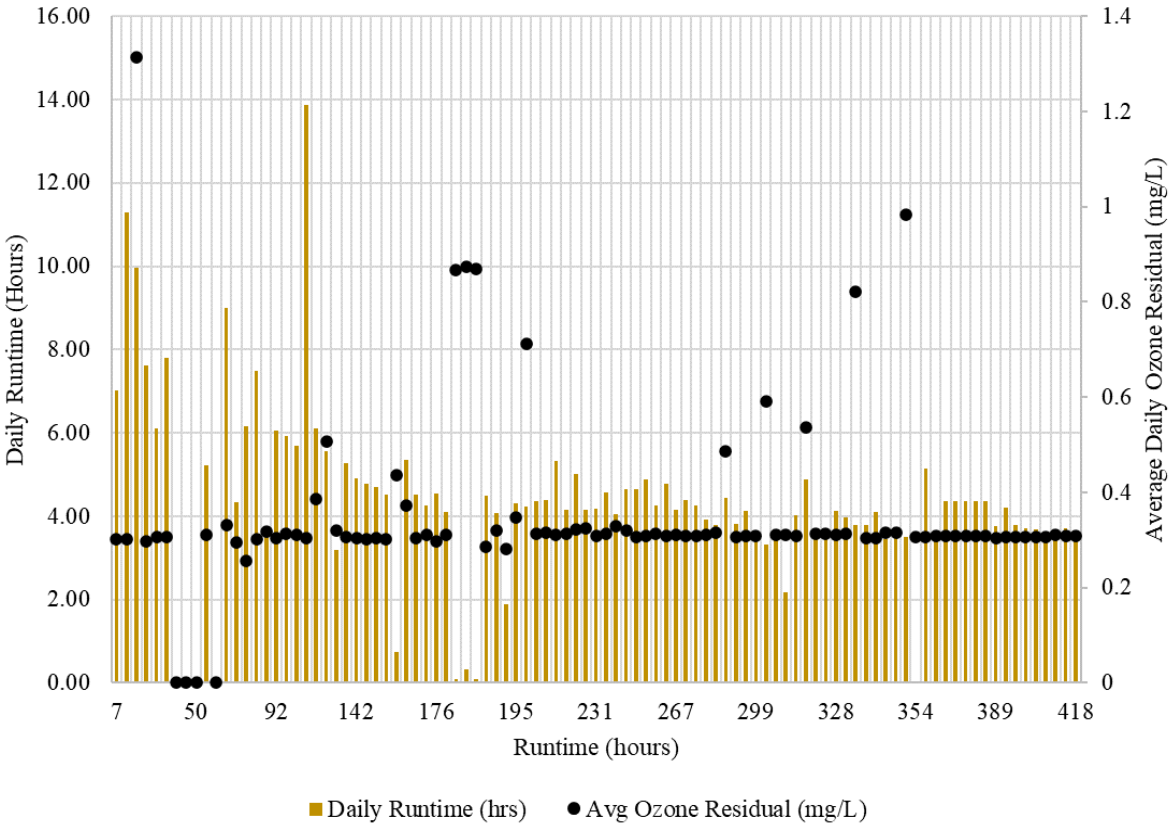

Figure 5-9. Average Daily Runtime and Ozone Residual of the Ozone Skid

Over the duration of the study, the pilot averaged a daily runtime of 4.4 hours at an average of 0.37 mg/l O_3 residual and 7.2 mg/l O_3 dose. Operation of the pilot was prevented periodically over academic and holiday breaks due to complications attributed from a low flow demand due to low campus population. Such events would occur at periods when the GST had reached volumetric

capacity, resulting in the groundwater wells and ozone skid to turn off. Additionally, personnel were not available to manage the pilot at all hours of the day, resulting in an inability to restart the pilot after early shut-offs. However, the pilot was prevented from being inoperable for more than three consecutive days as to avoid stagnation of carbon within the pilot columns. The pilot also did not operate on February 9, 2021, which occurred because the pilot turned off immediately upon start-up due to low oxygen purity. Important parameters required to further understand the flow conditions of the pilot columns, such as the designed empty bed volume (EBV), empty bed contact time (EBCT) and loading rates (flux) of the pilot columns are displayed in Table 5-4.

Table 5-4: Parameters of Operation for GAC Pilot Columns

Column	Media Height (in)	Column Dia. (in)	EBV (gal)	Average Flow Rate (gpm)	EBCT (min)	Flux (gpm/ft^2)
HPC-830	18.0	3.00	0.551	0.156	3.53	3.18
FS-400	18.0	3.00	0.551	0.155	3.56	3.15

At a designed empty bed volume of 0.55 gallons and an average flow rate of approximately 0.15 gpm, the resulting EBCT and flux for the HPC-830 and FS-400 pilot columns were 3.53-min and 3.56-min, and 3.18 gpm/ft^2 and 3.15 gpm/ft^2, respectively. As such, operational flow parameters for both carbon columns remained close throughout the entirety of the pilot study. The monthly flows for either pilot columns can also be observed in Table 5-5.

Table 5-5: Monthly Flow of GAC Pilot Columns

Carbon Column	November 21–30 Flow (gal)	December 1–31 Flow (gal)	January 1–31 Flow (gal)	February 1–25 Flow (gal)
HPC-830	357	1156	1280	845
FS-400	336	1133	1283	827

In terms of monthly flow, the pilot columns received the most flow in January. Additionally, the average daily flow loaded onto the HPC-830 and FS-400 pilot columns were both approximately 39 gallons per day. Through combination of the designed EBV for either pilot column and the monitored daily flow, the cumulative flow applied the pilot carbon columns in terms of EBVs is shown in Figure 5-10.

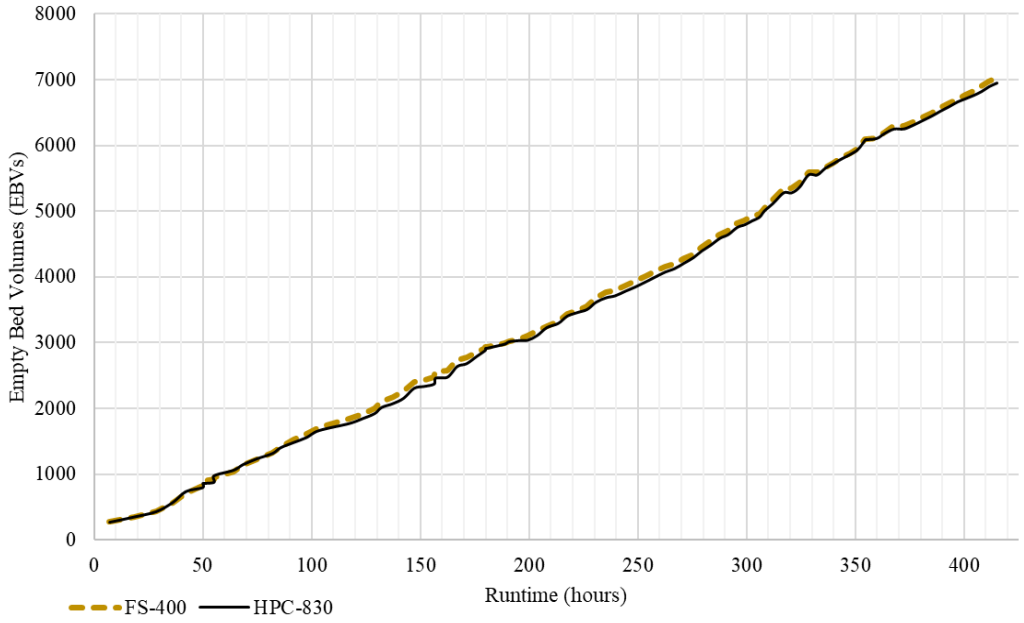

Figure 5-10: Flow in terms of EBVs for both GAC Columns in the Ozone-GAC Study

The daily flow regime for the pilot columns appear to be constant and in close relationship, however impacts to the daily flow due to low or zero flow events are observable in Figure 5-10. The HPC-830 and FS-400 pilot columns operated at a daily average of 72 EBVs and 73 EBVs, respectively, and ultimately operated for 7025 EBVs and 6950 EBVs, respectively. It is to be noted that the official starting date for the study does not begin at zero EBVs in Figure 5-10 because the pilot was running discontinuously for about two weeks during the pilot start-up period, which occurred from November 11, 2020 to November 21, 2020.

Water Quality Results

Listed in Table 5-6 are the resulting ranges of general water quality parameters monitored from the pilot over the duration of the piloting period through the procedural methodology and frequency explained in Chapter 4 for the UCF groundwater (Raw Well), ozone skid and both GAC pilot column sampling locations.

Table 5-6: Ranges for Water Quality Conditions for the Ozone-GAC Pilot

Parameter	Raw Well	Ozone Skid	HPC-830	FS-400
pH	7.36 – 7.79	7.37 – 7.76	7.18 – 7.71	7.20 – 7.71
Temperature (^oC)	18.8 – 26.4	24.4 – 29.2	24.2 – 30.5	24.5 – 30.6
Conductivity (mS/cm^2)	288 – 430	294 – 359	289 – 339	252 – 341
Ozone Residual (mg/L)	-[1]	0.23 – 0.71	0.00 – 0.05	0.00 – 0.05
Dissolved Oxygen (mg/L)	0.72 – 0.10	19.9 – 30.9	18.2 – 28.8	18.4 – 29.4
Alkalinity (mg/L)	131 – 173	131 - 175	138 - 177	138 - 170
Sulfide (mg/L)	0.26 – 1.42	0.00 – 0.06	0.00 – 0.01	0.00 – 0.01
Turbidity (NTU)	0.16 – 0.94	0.13 – 1.25	0.10 – 0.49	0.08 – 0.40
Bromide (mg/L)	< 0.20	< 0.20	< 0.20	< 0.20
Sulfate (mg/L)	2.19 – 4.82	3.91 – 5.89	4.05 – 5.91	3.99 – 5.85
ORP (mV)	-222 – -38	185 – 401	186 – 301	185 – 294
Iron (mg/L)	< 0.005 – 0.0212	< 0.005 – 0.0211	< 0.005	< 0.005
Magnesium (mg/L)	6.33 – 7.93	6.32 – 7.89	6.50 – 7.96	6.28 – 7.97
Calcium (mg/L)	40.3 – 49.3	40.2 – 49.1	39.6 – 48.8	40.1 – 48.8

[1]: Ozone residual for the raw well line was not taken.

Iron, magnesium, calcium, alkalinity, pH, bromide, and conductivity were unaffected by the pilot at each of the sampling locations over the entire period of study. Ozonation of the groundwater increased the levels of ORP, DO, dissolved ozone residual, temperature, and sulfate concentration, and decreased the concentration of sulfide. As reflected in the water quality results, the ORP of

the ozone skid was maintained from 200 mV to 300 mV to promote proper oxidation of the groundwater and prevent issues associated with carbon deterioration in the pilot columns. GAC filtration then further reduced the turbidity, ORP, temperature, dissolved ozone residual and DO of the supplied water.

The temperature was increased by the ozone skid on average by 19% as compared to the raw groundwater supply, resulting the water in the ozone skid to reach up to 30^{o}C periodically and decrease the efficiency of ozone solubility. This was remedied by increasing the amount of wasted flow, which allowed for more water to cycle in and out of the ozone skid and reduce the increase in contact tank water temperature. Contacting in the GAC columns would also further reduce the water temperature on average by 2% and 3% for the HPC-830 and FS-400 columns as compared to the influent from the ozone skid. Turbidity monitored from the ozone skid had increased on average by 25% as compared to the raw well water, and such an increase in turbidity was most likely caused by bubbles attributed to the oversaturation of DO in the contact tank. The degradation of aqueous ozone oversaturated the water in the contact tank and GAC columns with DO, resulting in the concentration of DO in either sampling location to range from 18 to 31 mg/l in the contact tank depending on the operating conditions of the ozone generator. Effluent from the HPC-830 and FS-400 columns also averaged a 7% and 6% reduction in their respective DO concentrations as compared to the ozone skid. Turbidity from the ozone skid was then reduced by the HPC-830 and FS-400 columns on average by 57% and 65%, respectively. Sulfide was consumed by the oxidation of the water by ozone, which is evident in the minor increases to the observed sulfate concentration post-ozonation and the 97% removal of total sulfide in the effluent of the ozone skid.

DBP Precursor Results

The determination of DBP precursor reduction by the integrated ozone-GAC pilot was completed through the monitoring of DOC and UV_{254}. SUVA was then calculated after the fact with the previously investigated DOC and UV_{254} measurements to determine the organic fractionation. To understand the relationship between the DOC and UV_{254} measurements taken from the pilot columns over the duration of the study, the relation was plotted for the HPC-830 and FS-400 pilot columns, as shown in Figure 5-11 and Figure 5-12.

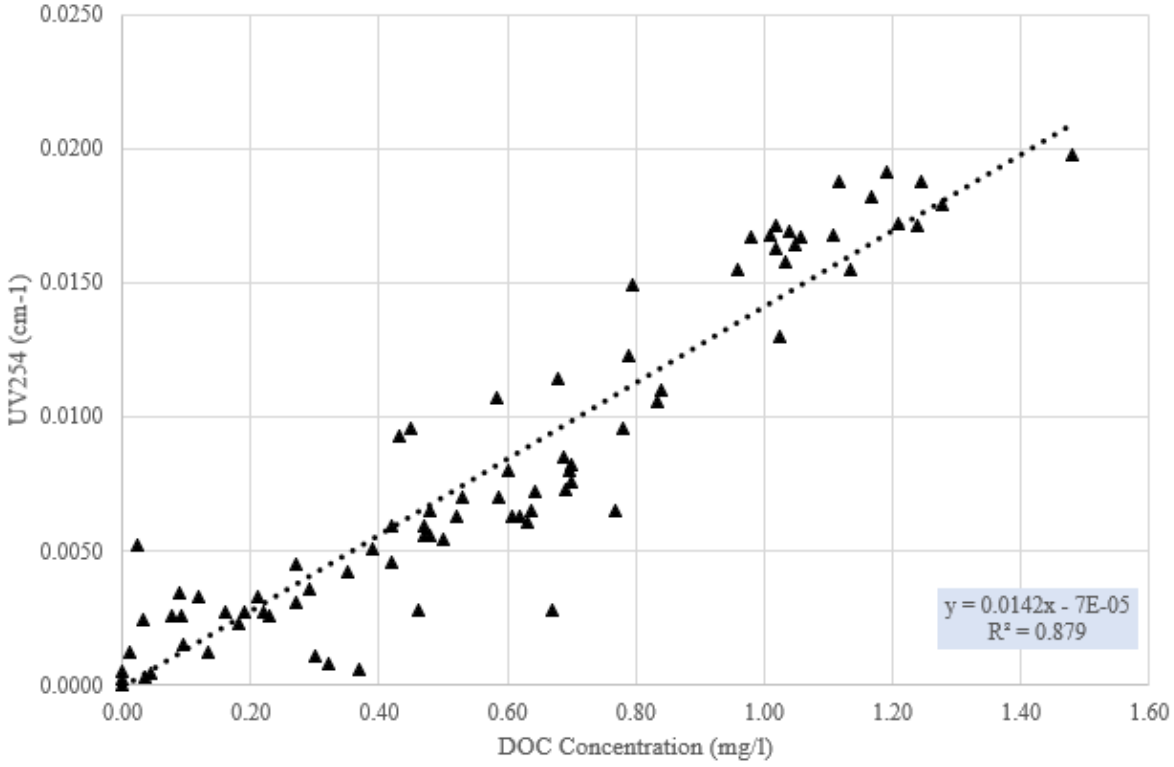

Figure 5-11: Relativity of DOC vs UV_{254} for the HPC-830 Pilot Column

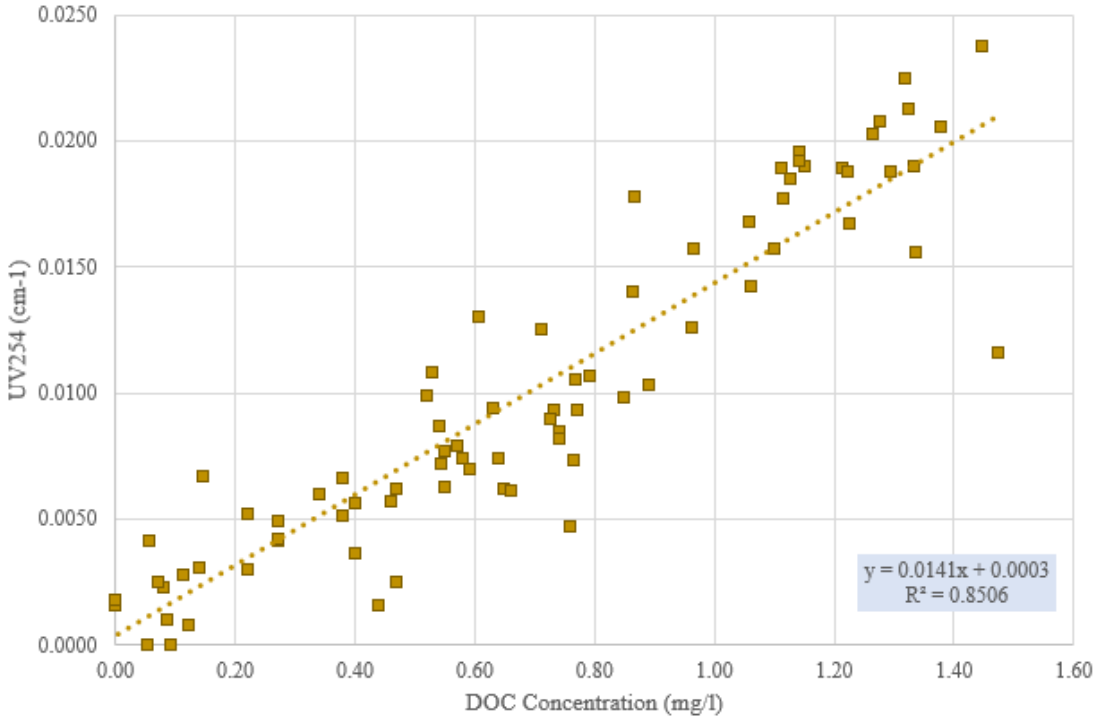

Figure 5-12: Relativity of DOC vs UV_{254} for the FS-400 Pilot Column

The relationship between DOC and UV_{254} in natural waters is very close (Brandstetter and Sletten, 1966). The reported r-squared value for HPC-830 and FS-400 columns were 0.879 and 0.851, resulting in a positive correlation between the NOM results for the integrated ozone-GAC study. Additionally, the DOC and UV_{254} results as monitored from the UCF groundwater, ozone skid and two GAC pilot columns in terms of runtime are presented in Figure 5-13 and Figure 5-14.

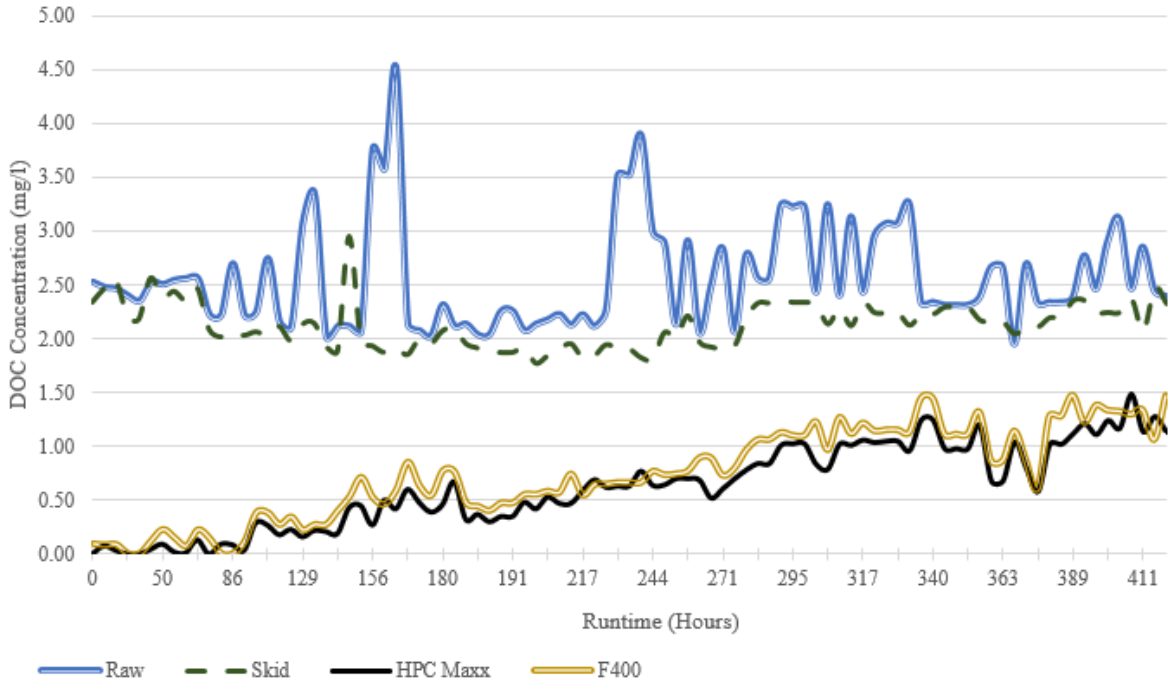

Figure 5-13: DOC Concentration Results from the Integrated Ozone-GAC Pilot Study

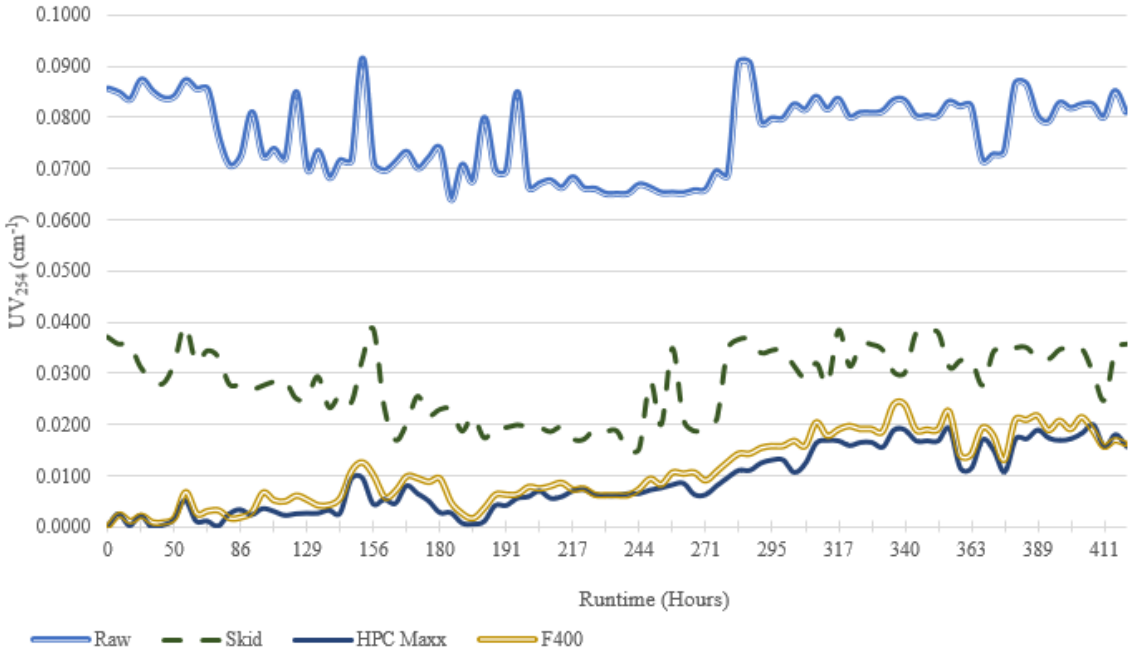

Figure 5-14: UV_{254} Results from the Integrated Ozone-GAC Pilot Study

Fluctuations observed in the resulting DOC and UV_{254} measurements from the integrated ozone-GAC pilot are due to the varying well water quality within the UCF wellfield. Performance of the ozone generator in reducing the DOC and UV_{254} of the influent flow was constant through the study, however the performance of the GAC columns to remove DOC and UV_{254} from the influent of the ozone skid decreased as the study progressed. Ozonation of the UCF groundwater water initially reduced the DOC and UV_{254} on average by about 0.42 mg/l and 0.048 cm^{-1}, respectively, resulting in initial reductions of approximately 20% and 63%. Ozonation of the groundwater was more efficient at reducing UV_{254} as compared to DOC, which would suggest that ozonation of the UCF groundwater was better suited to degrade the aromatic, UV absorbent fraction of NOM supplied in the UCF groundwater as opposed to the non-humic fraction or organics. Further treatment of the ozonated water through GAC filtration with the HPC-830 and FS-400 pilot columns reduced the DOC and UV_{254} substantially, however the performance of the treatment decreased as the study progressed. This decrease in performance can also be observed through the DOC and UV_{254} breakthrough curves for either pilot column, of which are included in Figure 5-15 and Figure 5-16.

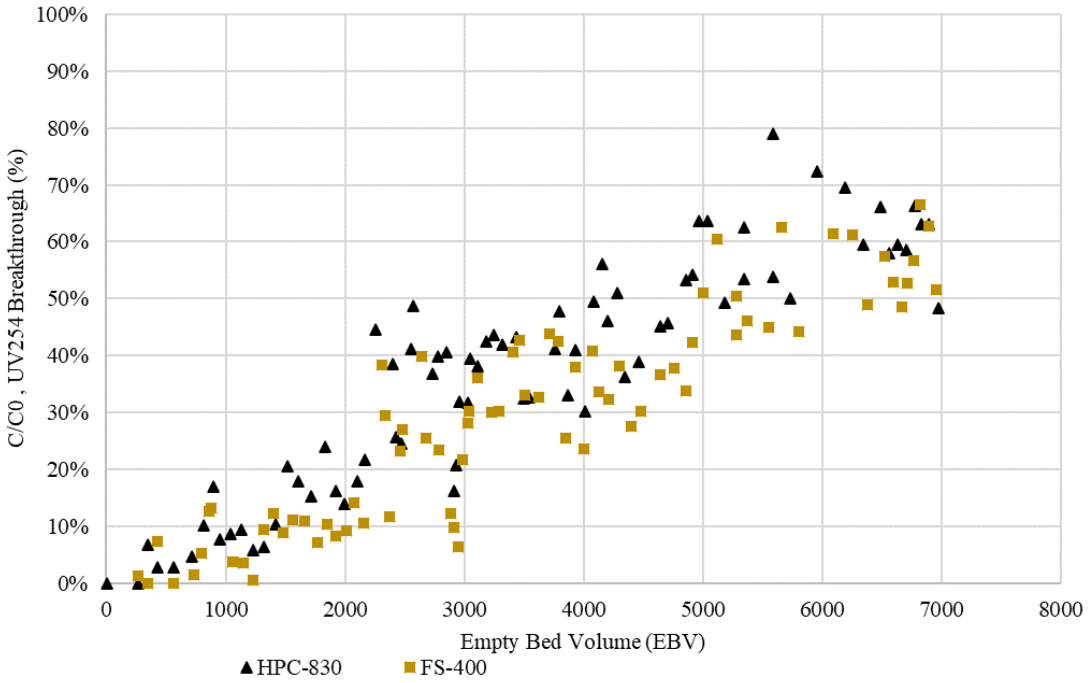

Figure 5-15: GAC Column Breakthrough of UV_{254} from the Integrated Ozone-GAC Pilot Study

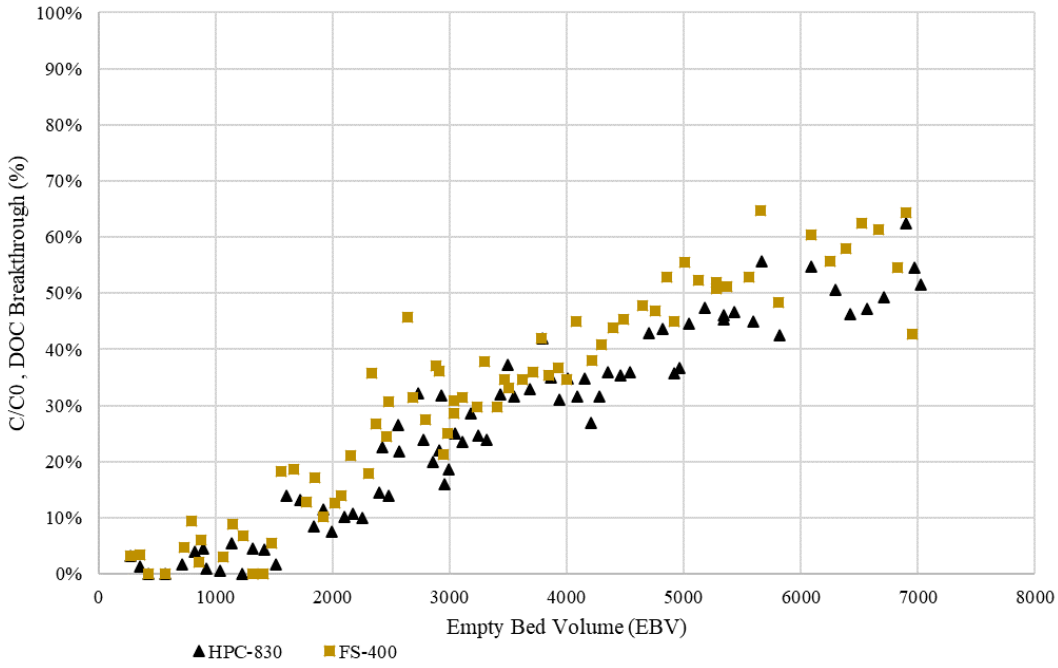

Figure 5-16: GAC Column Breakthrough of DOC from the Integrated Ozone-GAC Pilot Study

Breakthrough was observed in units of cumulative EBVs and was calculated relative to the influent DOC and UV_{254} as observed from the ozone generator's contact tank through use of Equation 2-12. Initial breakthrough for either columns began at approximately 1500 EBVs. The HPC-830 pilot column surpassed 50% DOC breakthrough at 5700 EBVs and 50% UV_{254} breakthrough at 4100 EBVs, while the FS-400 pilot column surpassed 50% DOC and UV_{254} breakthrough at 5000 EBVs and 4900 EBVs. On average, effluent from the HPC-830 pilot column contained 0.0016 cm^{-1} more UV_{254} and 0.0869 mg/L less DOC than the FS-400 Carbon column. In the final 1000 EBVs of the study, the HPC-830 carbon column averaged 62% UV_{254} breakthrough and 52% DOC breakthrough while the FS-400 carbon column averaged 56% UV_{254} breakthrough and 57% DOC breakthrough. Additional pilot column treatment efficiency in terms of pilot column effluent DOC concentrations can be observed in Figure 5-17 and Figure 5-18.

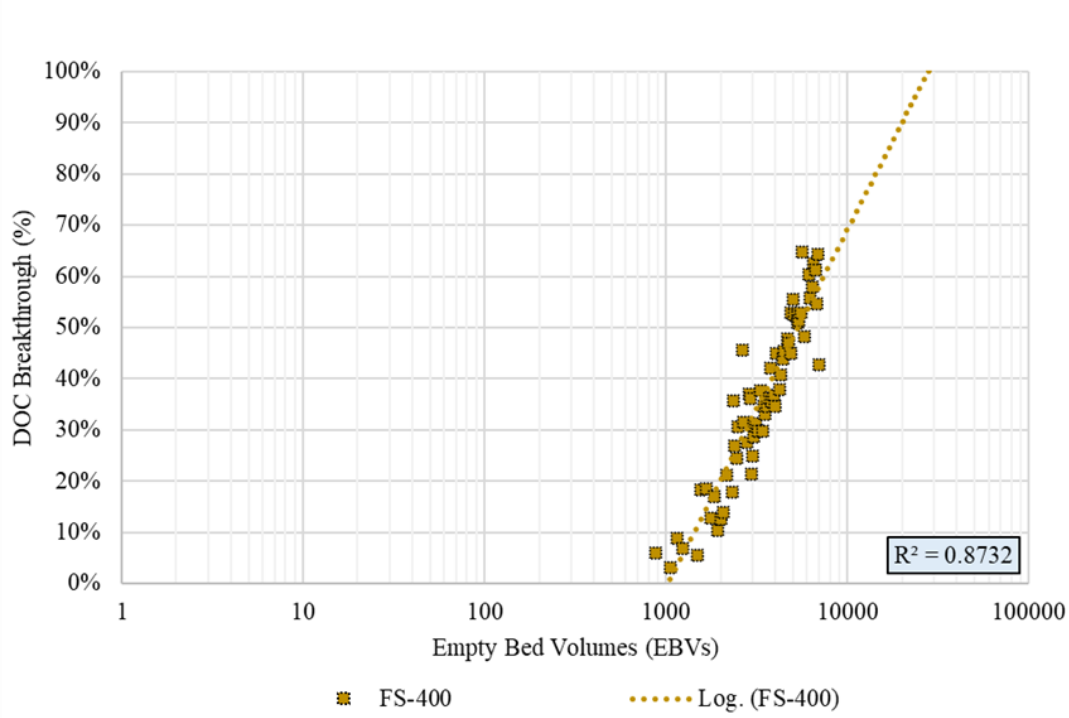

Figure 5-17: FS-400 Pilot Column Operation to DOC Exhaustion

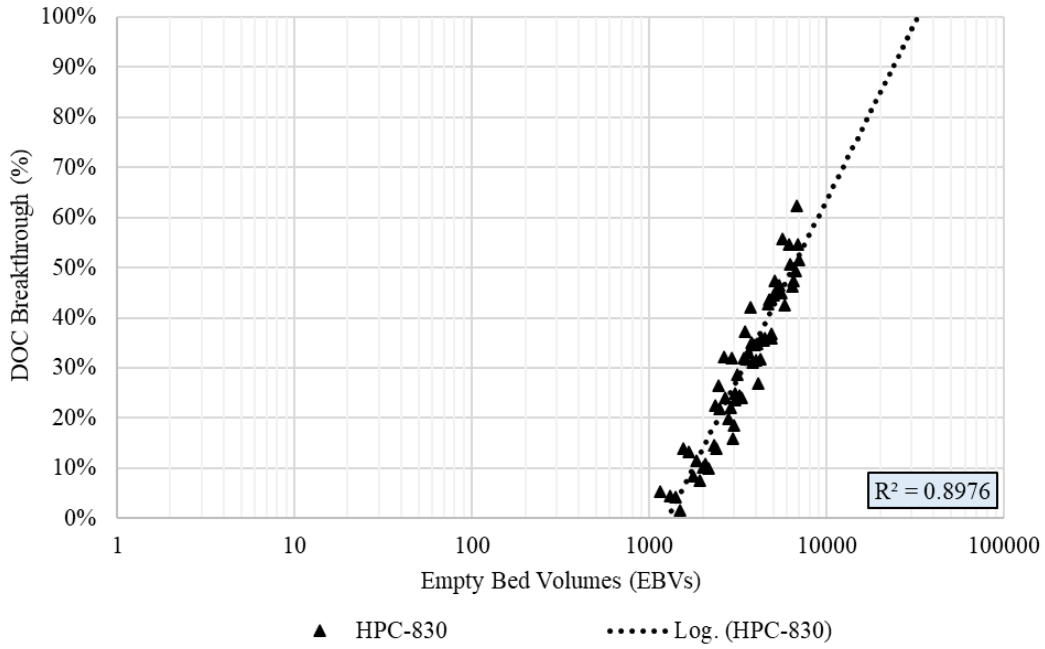

Figure 5-18: HPC-830 Pilot Column Operation to DOC Exhaustion

The FS-400 and HPC-830 pilot columns were estimated to be operable for approximately 30,000 EBVs and 35,000 EBVs prior to the occurrence of DOC breakthrough exhaustion. As such, the HPC-830 pilot column would exhaust soon after the FS-400 pilot column were to exhaust if both columns were allowed to operate for maximum bed volumes to reach total exhaustion. Additional pilot column treatment life-expectancy estimations in terms of pilot column effluent UV_{254} breakthrough over their extended uses can be observed in Figure 5-19 and Figure 5-20.

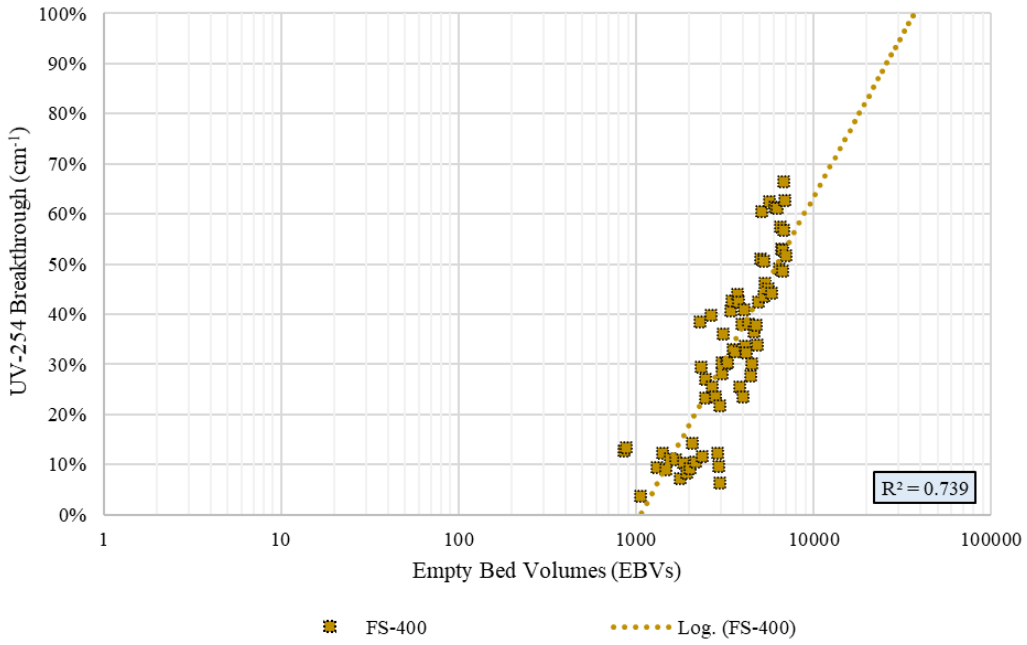

Figure 5-19: FS-400 Pilot Column Estimated Operation to UV_{254} Exhaustion

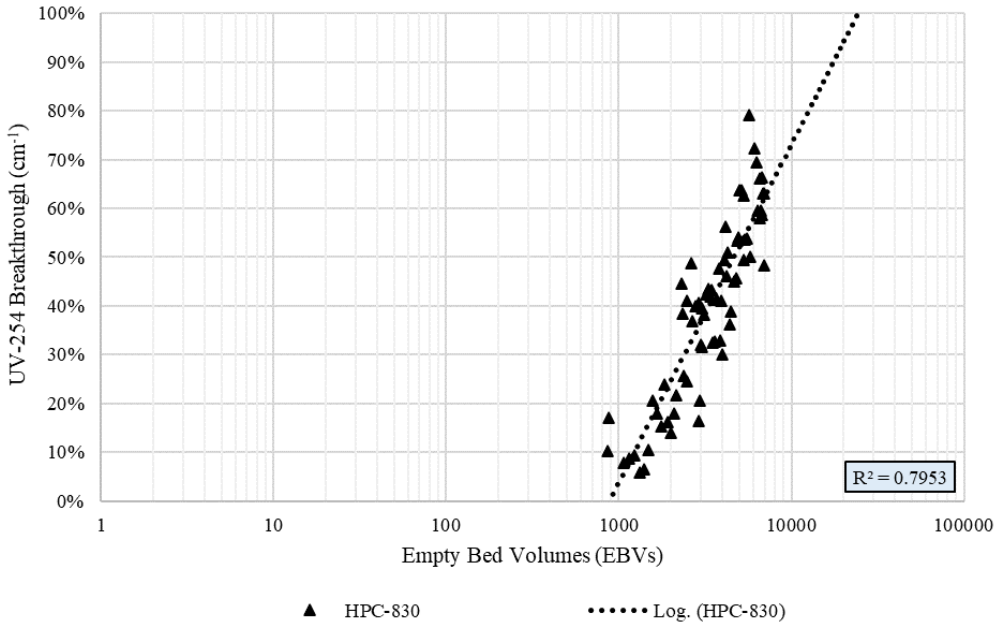

Figure 5-20: HPC-830 Pilot Column Estimated Operation to UV_{254} Exhaustion

The FS-400 and HPC-830 pilot columns were estimated to reach total bed UV_{254} exhaustion at approximately 35,000 EBVs and 25,000 EBVs, respectively. As such, the FS-400 pilot column would exhaust for UV_{254} breakthrough around 10,000 EBVs after exhaustion of the HPC-830 pilot column if both columns could operate for maximum bed volumes to reach total exhaustion. Further quantification of NOM for the piloted process can be observed in Figure 5-21, which displays the resulting SUVA results for the integrated ozone-GAC pilot at each of the sampling locations.

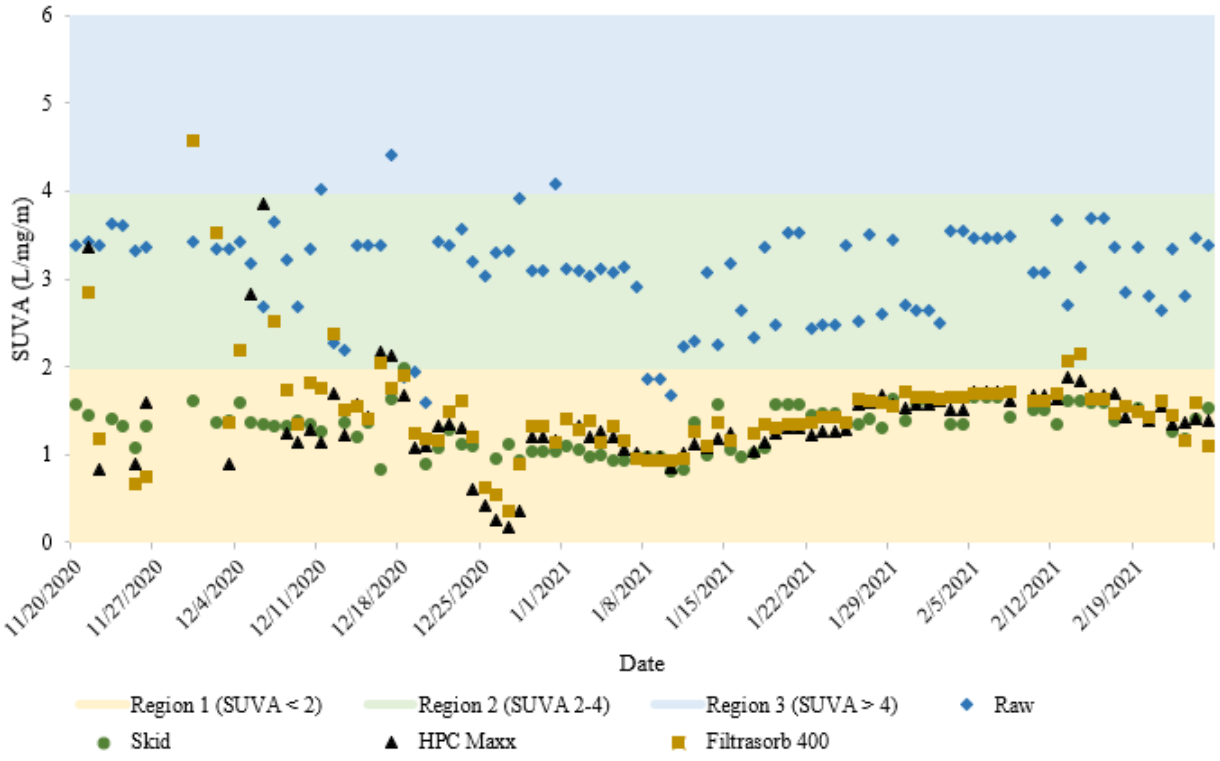

Figure 5-21: SUVA of the Integrated Ozone-GAC Pilot

SUVA results for the UCF groundwater would suggest that the water source mainly contained non-humic and humic organic matter during operation of the integrated ozone-GAC pilot. However, after ozonation and GAC filtration, the resulting SUVA values would suggest that the organic content of sampled water shifted to become more non-humic in content.. This would again suggest that the integrated ozone-GAC process has a high removal efficiency for humic organic matter and a low removal efficiency for non-humic organic matter. This difference in NOM treatability can potentially impact the formations of DBPs.

As such, the HPC-830 carbon column proved to be more efficient in reducing DOC while the FS-400 carbon column was more efficient in reducing UV_{254}. Additionally, the FS-400 pilot column is expected to treat both DOC and UV_{254} for around the same amount of EBVs. In contrast, the

HPC-830 pilot column is estimated to exhaust for UV_{254} well before it is to exhaust for DOC. This difference in treatability between different types of NOM fractions can have a large impact on the reduction efficiency for TTHM formations. It would be suggested that the carbon type for the master planning of future UCF treatment systems be chosen with DOC treatability in mind, as oxidation of the supply will reduce a large fraction of humic organics in the supply, so DOC remediation will be a higher priority for the designed GAC contactors.

DBP Formation Results

Periodic DBP formation experimentation was conducted on aliquots sampled from the UCF groundwater, ozone contact tank, and both GAC pilot columns through the duration of the integrated ozone-GAC pilot study. The occurring dates for specific DBP experimentation conducted on the pilot can be viewed in Table 5-7. Additionally, water quality results for free chlorine, turbidity, temperature, and pH of the samples studied during DBP experimentation are included in APPENDIX A.

Table 5-7: Dates of DBP Experimentation for the Ozone-GAC Pilot Study.

DBP FP Sample Date	**TTHM**		**HAA5**
	24-hr Formation	48-hr Formation	48-hr Formation
November 23rd	-	X	X
January 13th	-	X	X
January 18th	G/O/X	G/O/X	O/X
January 27th	G/O/X	G/O/X	O/X
February 8th	X	X	X
February 15th	X	X	X
February 24th	X	X	X

G: UCF Aerated Groundwater; O: Ozone Generator; X: Pilot Column

TTHM and HAA5 formation at 48-hours of incubation were monitored through the entirety of the study to observe the changes in the reduction of DBPs after ozonation and GAC filtration. Formation of TTHMs at 24-hours of incubation were also monitored for the GAC columns for the second half of the study. The average chlorine residuals for the aerated UCF groundwater, ozone generator effluent (ozone skid) and two GAC pilot columns at 24-hours and 48-hours of incubation at 30^{o}C are included in Table 5-8.

Table 5-8: Chlorine Reduction of the Integrated Ozone-GAC Pilot

Sample	Dose (mg/l Cl_2)	0-hr Residual (mg/l Cl_2	Initial % CL_2 Reduction	24-hr Residual (mg/l Cl_2)	% CL_2 Reduction at 24-hr	48-hr Residual (mg/l Cl_2)	% CL_2 Reduction at 48-hr
Raw[1]	7.3	2.7	63	0.67	91	0.23	97
Ozone Skid	5.2	2.5	51	1.1	78	0.58	89
HPC-830	3.9	2.1	47	1.6	60	1.2	69
FS-400	3.8	2.0	48	1.1	71	0.90	76

[1]: *Raw results indicate formation potential results for the UCF groundwater supply.*

Ozonation and GAC filtration of the UCF groundwater greatly reduced the required chlorine dose to supplement a residual between 0.20 mg/l Cl_2 to 1.00 mg/l Cl_2. On average, the integrated process required 3.4 mg/l Cl_2 less than the UCF groundwater, and 1.3 mg/l Cl_2 less than the ozone generator effluent. After 48-hours of incubation, the average chlorine residual from the raw, HPC-830 and FS-400 column samples were reduced by 97%, 69% and 76%, respectively. Implementation of an integrated process would drastically reduce the required amount of chlorine that UCF would have to introduce to the water supply, which would suggest that DBP formation in the PWS and costs associated with the purchasing of chemicals would both be reduced. Additionally, the integrated process would allow for a more sustainable chlorine residual in the UCF PWS, as the decay of chlorine residual from the pilot column effluent encountered less reduction than the raw and

ozonated samples. Average TTHM and HAA5 formations at 24-hours and 48-hours of incubation are included in Table 5-9.

Table 5-9: DBP Formation Experimentation Results of the Integrated Ozone-GAC Pilot Study

Sample	Average Chlorine Dose	Average TTHMs		Average HAA5s
	Dose (mg/l Cl_2)	24-hr TTHM Formation (ppb)	48-hr TTHM Formation (ppb)	48-hr HAA5 Formation (ppb)
Raw[1]	7.3	83	95	40
Ozone Skid	5.2	75	91	44
HPC-830	3.9	42	46	19
FS-400	3.8	49	54	22

[1]: Raw samples were collected from the UCF well influent line and aerated overnight.

As compared to the average formations of TTHMs and HAA5s observed from the chlorinated and aerated UCF groundwater, the ozone generator effluent, HPC-830 and FS-400 pilot columns reduced the formation of TTHMs at 48-hours of incubation on average by 4.2%, 49% and 43%, respectively. The formation of HAA5s at 48-hours of incubation were also reduced on average by the HPC-830 and FS-400 pilot columns by 52% and 43%, respectively. Before being treated by the integrated process, the formation potential for TTHMs of the aerated groundwater exceeded the MCL for TTHMs by approximately 15 ppb. Post-treatment by the integrated process, TTHM formation was reduced by half. Additionally, the HAA5 formation potential of the aerated groundwater was already under the MCL; however, the integrated process was also able to reduce its formation by half. Displayed in Figure 5-22 are the speciation of THMs analyzed from DBP experimentation completed on sampled effluent from the pilot columns over the course of the integrated study.

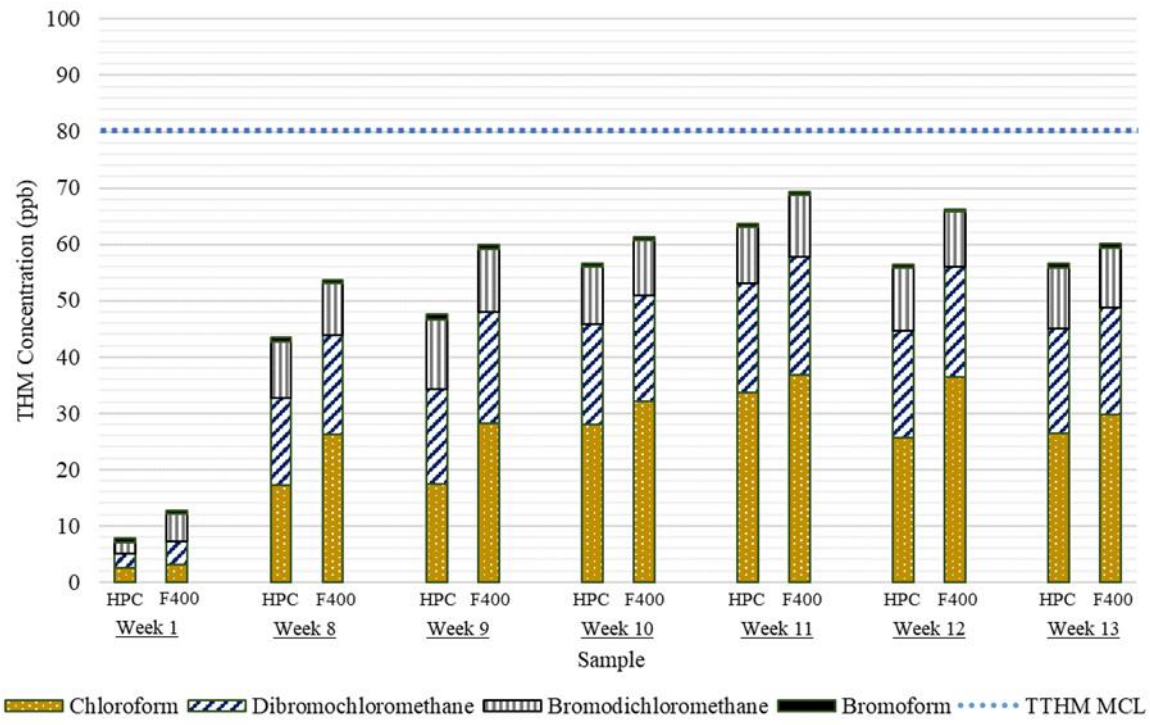

Figure 5-22. THM FP and Speciation for the Integrated Ozone-GAC study at 48-hours

The general water quality and DBP formation potential of the aerated UCF groundwater used as reference for the analysis can be found in APPENDIX A. The major speciation of THMs from the effluent of the pilot columns was chloroform, followed closely by DBCM. This would suggest that trace amounts of bromide in some form are available in the supply, however they are not available in a high enough concentration to form brominated DBPs in large quantities. Formation of TTHMs at 48-hours of incubation analyzed from effluent from the FS-400 pilot column were consistently higher than formations observed from effluent of the HPC-830 column by an average of 16%, or 7.2 ppb. Additionally, effluent from both pilot columns remained below the MCL for TTHMs throughout the entirety of the study. Initial TTHM analysis on the pilot column effluent revealed formations of TTHMs below 10 ppb. However, after seven weeks of operation the formation of TTHMs at 48-hours of incubation had increased to approximately 43 ppb and 54 ppb for the HPC-

830 and FS-400 pilot columns, respectively. After Week 8 and beyond the surpassing of 50% DOC and UV_{254} breakthrough, effluent from both pilot columns contained formations of TTHMs which remained between 40 ppb and 70 ppb. This plateauing in column TTHM formation may display a shift from adsorption to biological mode of treatment by the columns, however further analysis was not completed. Additionally, the average reduction of TTHMs from the effluent of the HPC-830 and FS-400 pilot columns after Week 8, as compared to the average groundwater formation potential results collected in mid-January, 2021, were 54 ppb and 62 ppb, respectively. On average, and in relation to the influent stream, the HPC-830 column removed 44% of TTHMs and 38% of HAA5s, while the FS-400 column removed 40% of TTHMs and 26% of HAA5s at 48-hours of incubation. The reduction of individual THM speciation formations observed from the HPC-830 and FS-400 pilot column effluents can also be observed in Figure 5-23 and Figure 5-24.

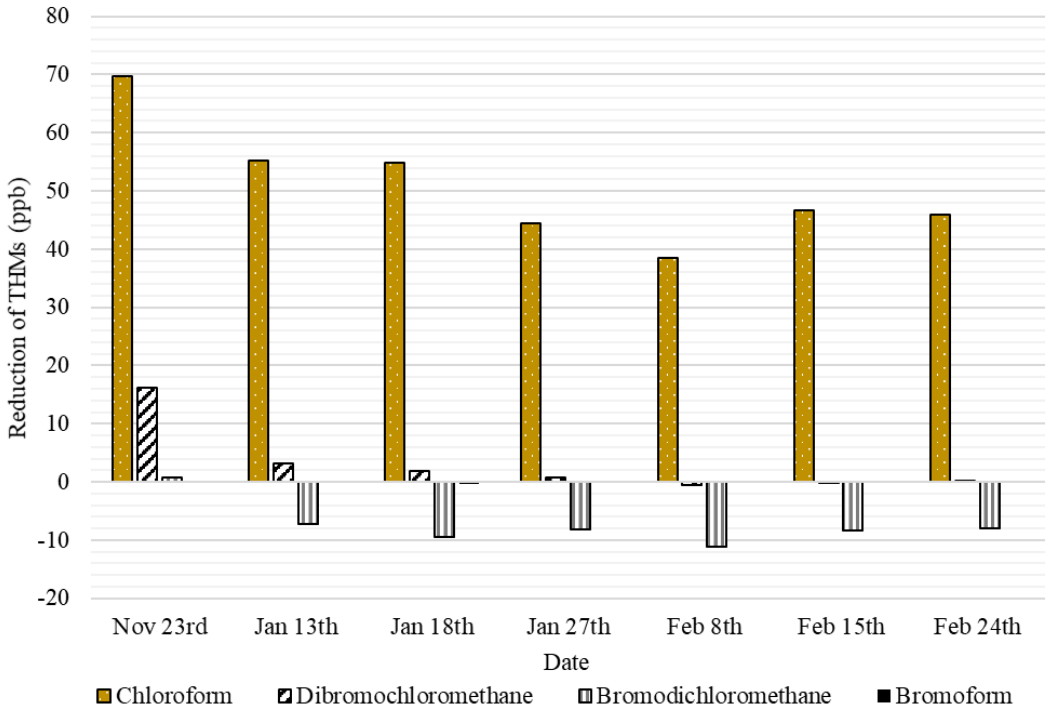

Figure 5-23: Impact on THM Speciation by the HPC-830 Pilot Column

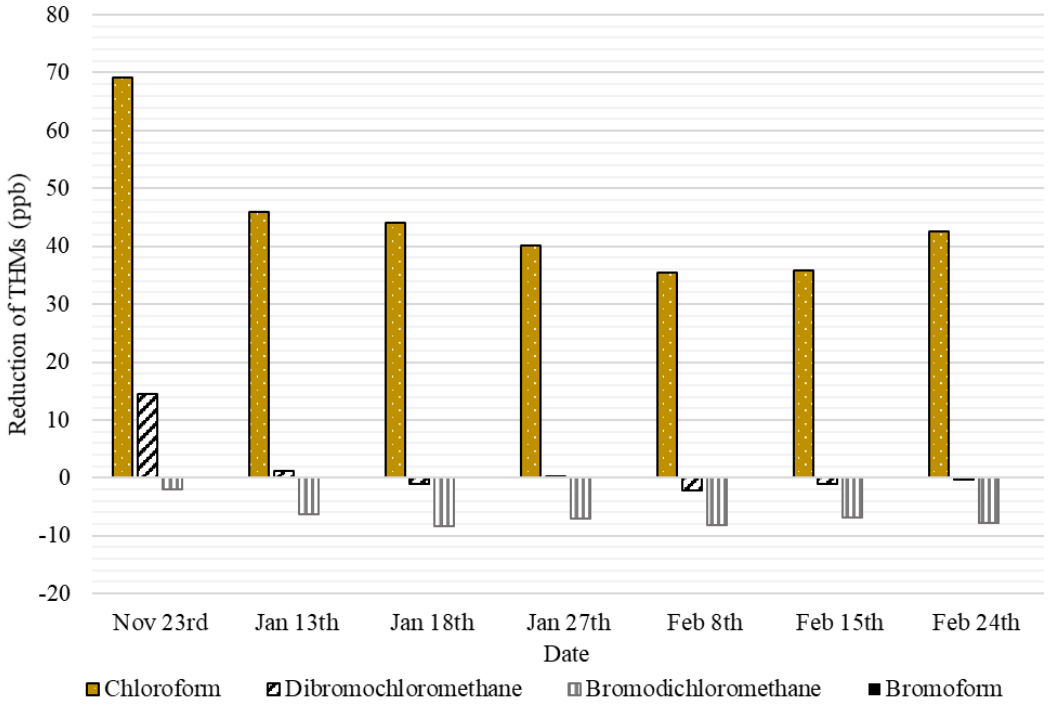

Figure 5-24: Impact on THM Speciation by the FS-400 Pilot Column

Concentrations are shown as either a positive concentration, displaying a removal of the constituent after treatment, or a negative concentration, displaying an increase in the constituent after treatment. It is to be noted that formations of bromoform were detected below the MDL of the instrument (at > 0.7 ppb) so conclusions on the removal proficiency of the integrated process for the compound could not be made. Chloroform was discovered to be the THM with the highest removal rate and BDCM was found to be added to the system after treatment by the integrated treatment process pilot. From Week 1 to the Week 13, the removal efficiency by the integrated process for chloroform and DBCM was reduced from 70 ppb and 15 ppb to approximately 40 ppb and near zero, respectively. However, bromide analysis completed on the UCF groundwater shows that the ambient concentration of bromide in the supply was less than 0.005 mg/l, and the observed formations of brominated THMs in the DBP formation experimentation yielded results that would

align with these results. This would suggest that the risks to public health attributed from the consumption of brominated DBPs would be minimal. To determine the efficiency of either pilot column to reduce TTHMs over their extended use, relations between estimated TTHM formation concentrations at predicted EBVs of operation can be observed in Figure 5-25.

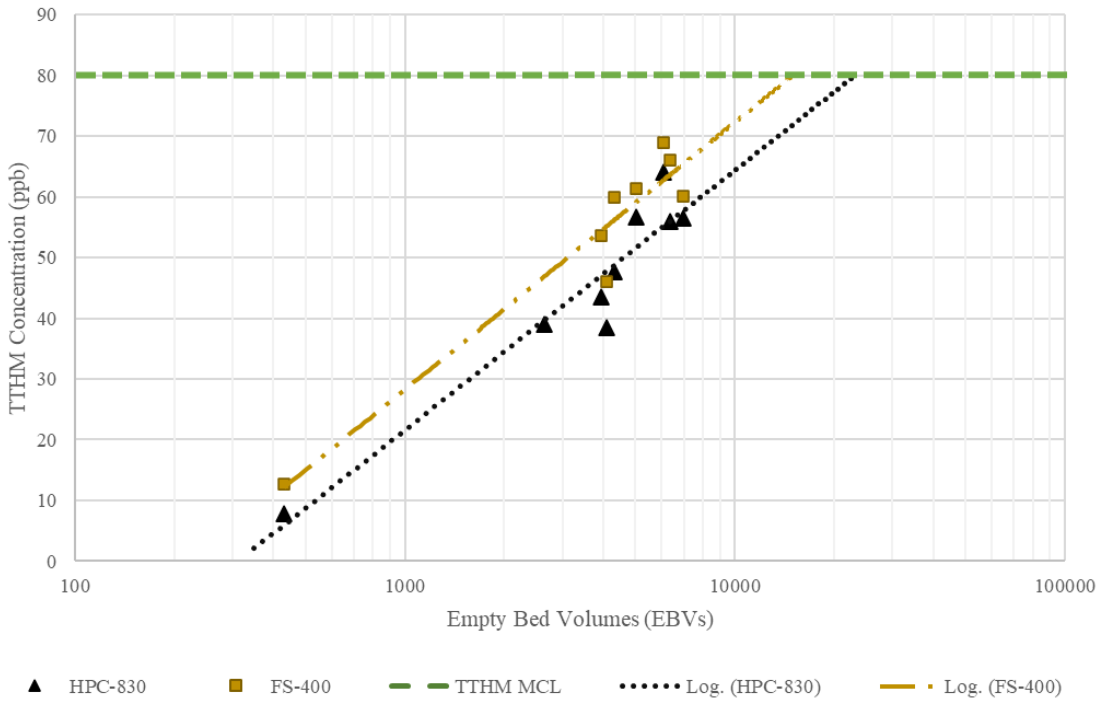

Figure 5-25: Pilot Column EBVs to TTHM Exhaustion

The FS-400 and HPC-830 pilot columns were also estimated to surpass the MCL for TTHMs at approximately 15,000 EBVs and 22,500 EBVs, respectively. This would suggest that the HPC-830 carbon type would be more efficient at reducing DBP formations for a longer period of operation as compared to the FS-400 carbon type if both columns were allowed to operate until total TTHM MCL exhaustion. To satisfy this claim, the TTHMs and coinciding DOC and UV_{254} measurements taken at the time of formation analysis for both carbon types are included in Figure 5-26.

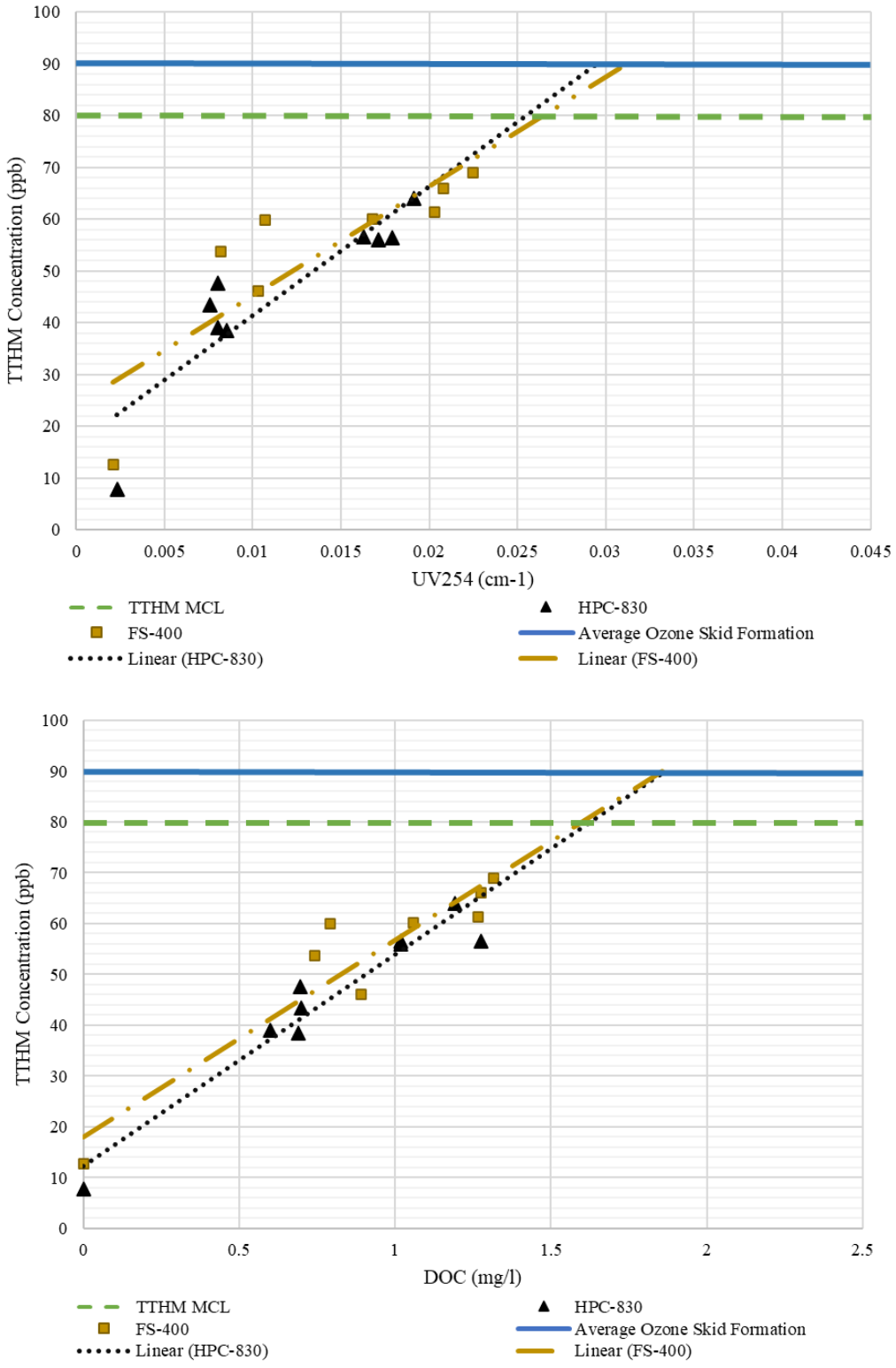

Figure 5-26: Pilot Column UV_{254} (above) and DOC (below) to TTHM Exhaustion

The average effluent DOC and UV_{254} values resulting from the ozone generator were 2.1 mg/l and 0.028 cm^{-1}, respectively. These observed values were in close approximation to the estimated pilot column DOC and UV_{254} values at TTHM exhaustion from Figure 5-26, which were 1.9 mg/l for both pilot columns and 0.030 cm^{-1} for the HPC-830 pilot column and 0.032 cm^{-1} for the FS-400 pilot column. As such, the estimations made in the previously estimated model of EBVs to TTHM exhaustion for either column is more probable, as the estimated DOC and UV_{254} levels at the time of exhaustion coincide with the actual effluent ozone generator NOM results. Additionally, the resulting 48-hour speciation and formation of HAA5s sampled throughout the duration of the integrated ozone-GAC study are included in Figure 5-27.

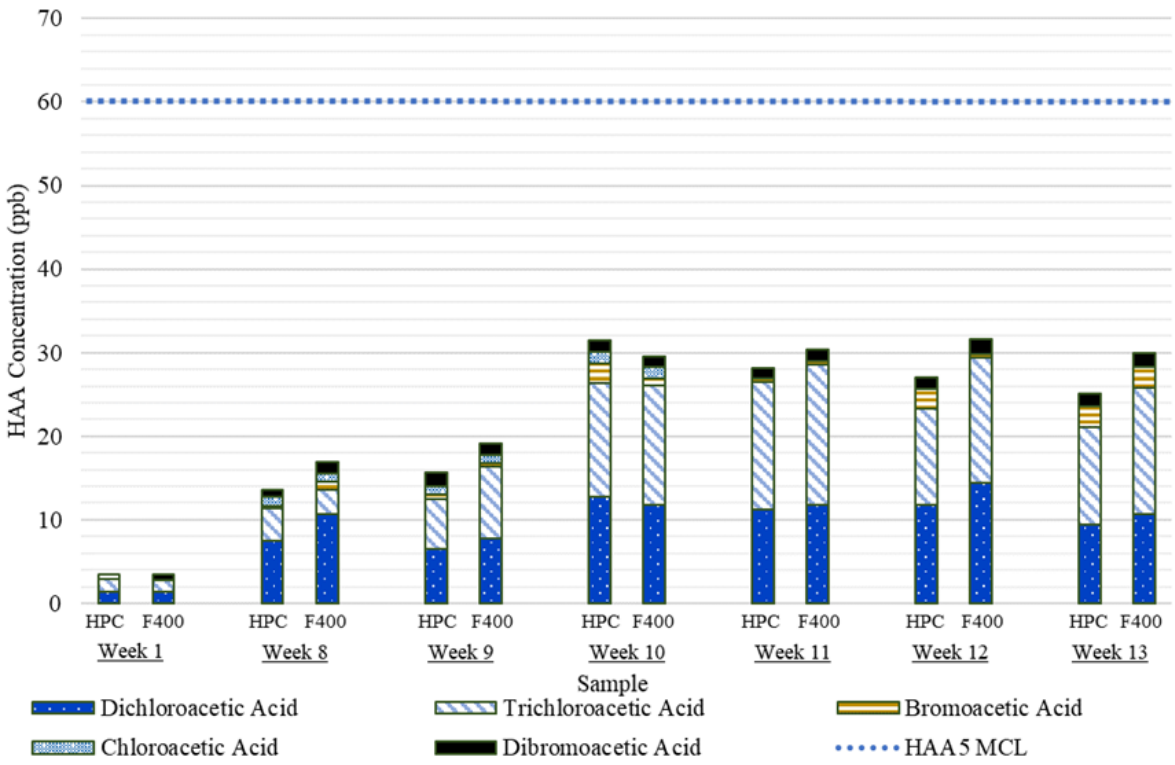

Figure 5-27: HAA Formation of the Integrated Ozone-GAC Pilot at 48-hours of Incubation

Effluent from the ozone generator averaged higher HAA5 concentrations as compared to the aerated UCF groundwater, however both sampling locations produced HAA5s below the MCL of 60 ppb. Initial DBP formation experimentation conducted on the effluent water of the pilot columns showed formations of HAA5s below the concentration of 5 ppb for either carbon type. From Week 8 to Week 10, a spike in HAA5 concentration had occurred during a coinciding rise in UV_{254} breakthrough, which rose from 35% to 50%. This spike in HAA5 concentration and UV_{254} breakthrough from approximately 4100 EBV to 5000 EBV (coinciding to approximately 200 to 300 hours of runtime) coincided to the HAA5 concentrations for the HPC-830 and FS-400 carbon columns increasing from 13 ppb to 32 ppb and 16 ppb to 30 ppb, respectively. During this same period, the formation of TTHMs increased from 43 ppb to 57 ppb for the HPC-830 column and from 54 ppb to 61 ppb for the FS-400 column. In the final four weeks and as compared to the average HAA5 formation potential of the aerated UCF groundwater, the HPC-830 column removed 38% of HAA5s at 48-hours of incubation, while the FS-400 column removed 26% of HAA5s at 48-hours of incubation. On average, the HPC-830 column was observed to reduce 1.7 ppb more HAA5s on average as compared to the FS-400 column. Further observations on the reduction of HAA5s by the integrated process for either pilot column can be observed in Figure 5-28 and Figure 5-29.

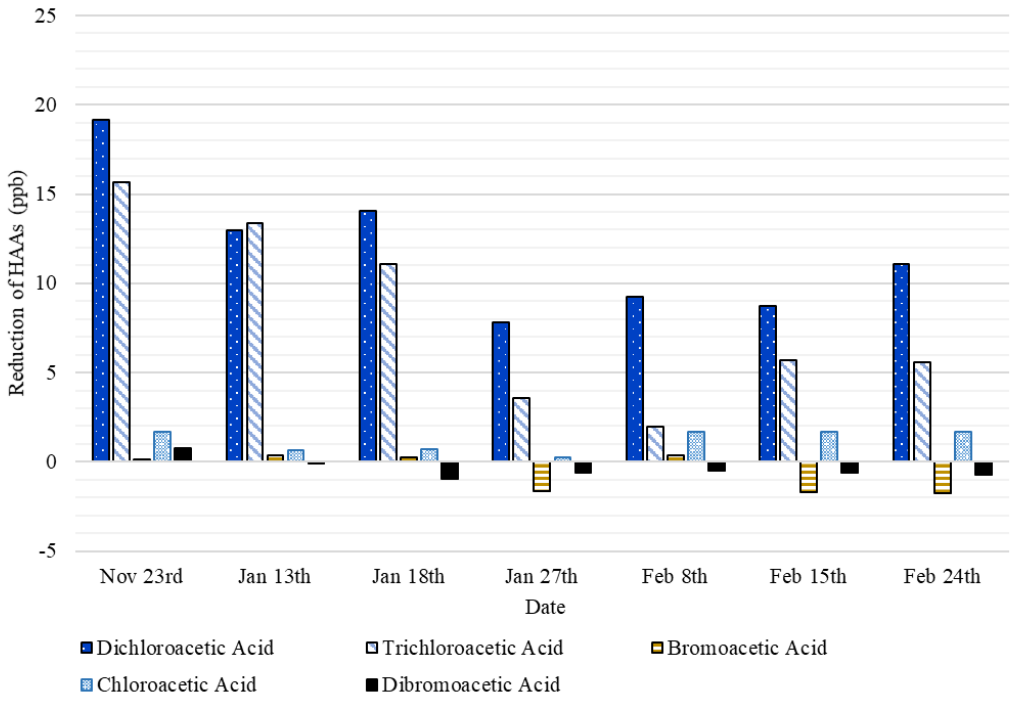

Figure 5-28: Impact on 48-hour HAA Speciation for the HPC-830 Pilot Column

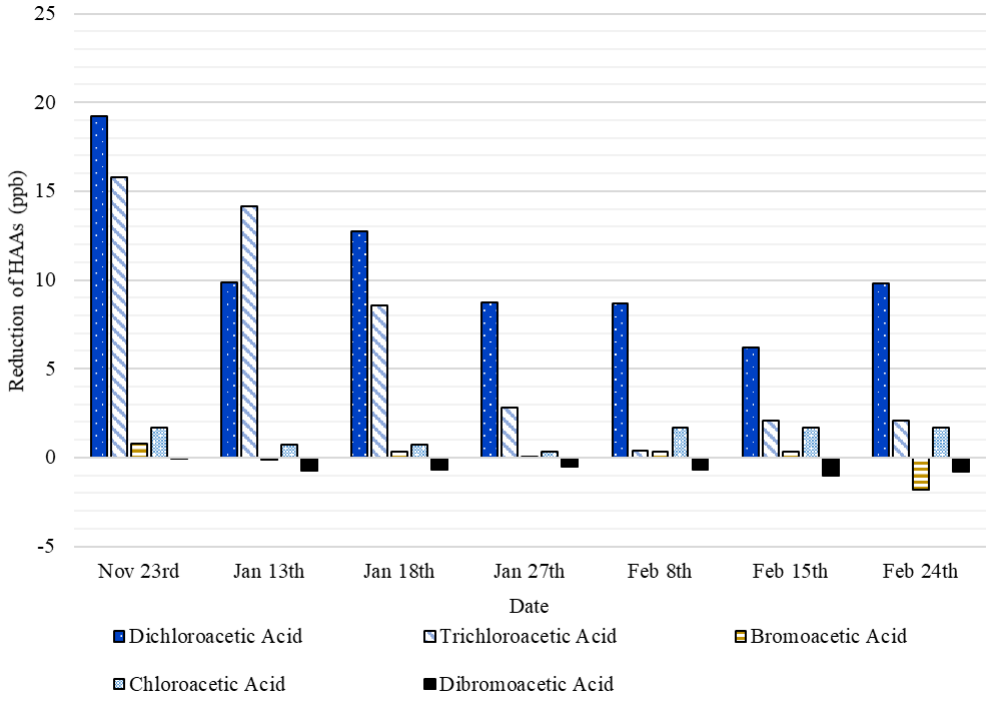

Figure 5-29: Impact on 48-hour HAA Speciation for the FS-400 Pilot Column

Removal efficiency for the main species of HAAs formed by the integrated process reduced as the study progressed for both pilot columns. From Week 1 to Week 8, the removal of TCA was sustained at approximately 15 ppb, however from Week 8 to Week 11, the removal efficiency of TCA fell from approximately 15 ppb to near zero for both pilot columns. Overall, the HPC-830 pilot column was more effective at removing HAA5s as compared to the FS-400 pilot column, however both pilot columns operated admirably to reduce formations of HAA5s to concentrations well below the MCL. From Week 8 to the end of the piloting period, both pilot columns were producing trace amounts of DBAA, however the formations did not exceed 5 ppb.

Carbon Results

Extended use of the pilot columns within a treatment system utilizing an advanced oxidation process through ozonation resulted in alterations to the chemical characteristics of the HPC-830 and FS-400 carbon types through impact to the hardness, iodine number and apparent density. Such changes for the top and bottom six inches of either pilot column can be observed in Table 5-10.

Table 5-10: Characteristics of Carbon Types at Start and Finish

Carbon Condition	Carbon Type		Iodine Number (mg/g)	Hardness (Abrasion Number)	Apparent Density (g/cc)
Virgin Carbon	HPC-830		1000 (min)	>80	0.27 (min), 0.37 (max)
	FS-400		1050 (min)	75	0.54
Exhausted Carbon	HPC-830	Top	860	60	0.37
		Bottom	790	79	0.57
	FS-400	Top	780	77	0.58
		Bottom	820	85	0.60

As compared between the top and bottom six-inches of either pilot column, the hardness of the HPC-830 and FS-400 carbon columns was reduced by 8 Abrasion Number (AN) and 19 AN. However, when compared to the stock characteristics of the carbon types, the hardness of the FS-400 column increased and the hardness of the HPC-830 decreased. The impact on hardness of the carbon could be attributed to the oxidizing capacity of the water, as the influent to the pilot columns carried a residual of ozone that was depleted by the time water exited the pilot columns. The iodine numbers of both carbon types were also reduced by 175 for the HPC-830 carbon type and 250 for the FS-400 carbon type. Apparent density of either carbon type also increased, with the bottoms of either pilot columns being denser than the top portions. This may have occurred because the flow of the system forced the fines from the tops to the bottoms of the pilot columns, compacting the carbon at the bottom. Impacts on the apparent density can also be attributed to the design of the pilot column casings themselves and may not be a factor when applied to full-scale application as GAC contactors retain different hydraulic characteristics. Additional changes to particle distribution for the top and bottom six inches of the pilot columns can be observed in Figure 5-30 and Figure 5-31.

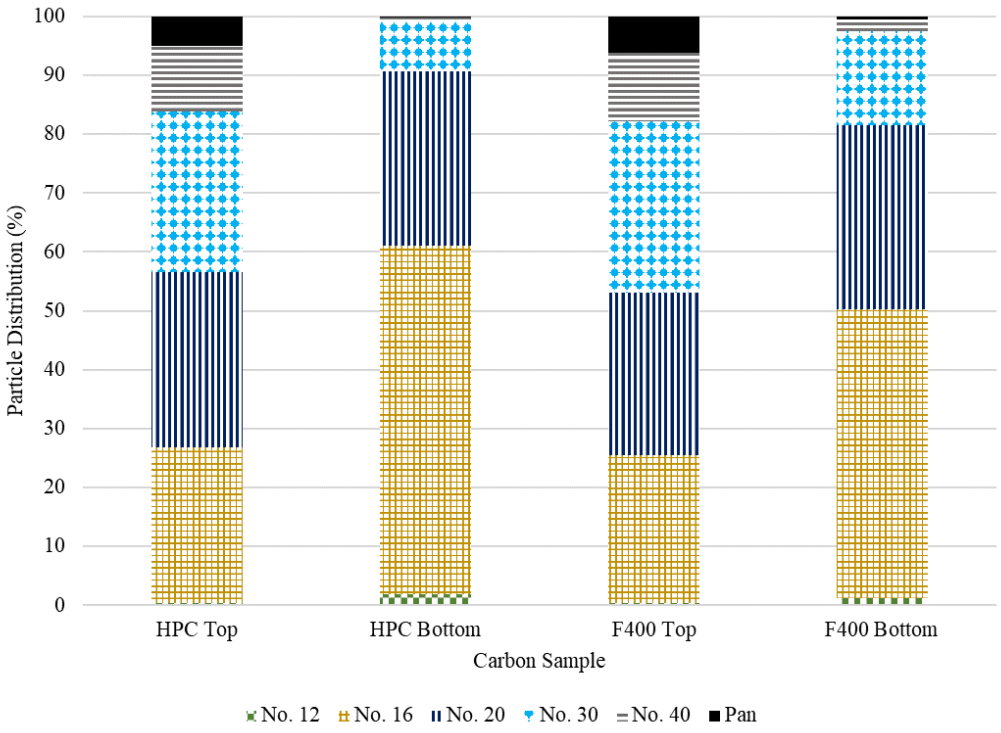

Figure 5-30: Exhausted Column Top and Bottom Particle Distributions

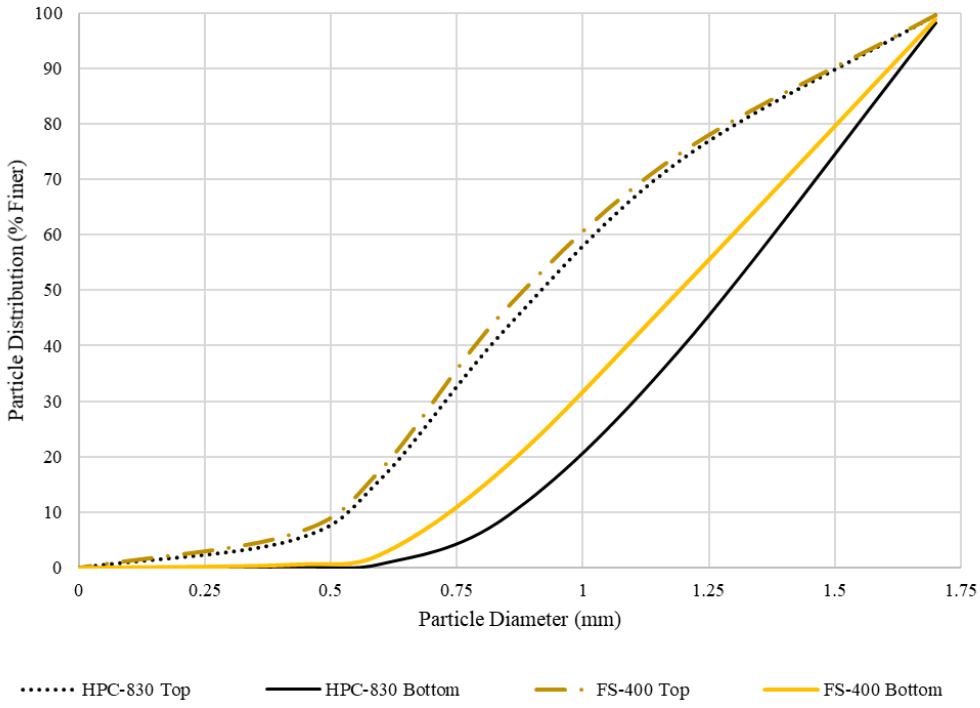

Figure 5-31: Exhausted Pilot Column Percent Finer Distribution Curves

Figure 5-30 and Figure 5-31 both reveal a shift of larger particles from the top to the bottom of the GAC pilot beds, and loss of small size carbon fines in the bottom sections of either pilot column. Additionally, the percent finer curves for the top sections of either carbon type display better "well-graded" profiles when compared to the percent finer curves of their associated bottom sections. This is perhaps because the columns were not backwashed during the ozone-GAC study period. Finer activated carbon particle sizes allow better access to the surface area and faster adsorption kinetics; however, a lower effective size will have a higher pressure drop and will filter smaller particles which can result in a higher backwash frequency compared to GAC with a higher effective size.

Quality Control and Quality Assurance

Quality control and quality assurance was completed for both studies presented in the prior results. Precision control charts for the DOC, UV_{254} and DBP formation results from the integrated ozone-GAC study can be observed in Figure 5-32, Figure 5-33, Figure 5-34 and Table 5-11, and for the stand-alone ozonation study can be observed in Figure 5-35, Table 5-12, and Table 5-13. Values above the warning and critical limits were due to the detection limits of monitoring equipment and other known factors, and the resulting values were not included in the prior analysis. Many UV_{254}, DOC and TTHM measurements that failed the precision control charts were also low level, which causes the data to be more prone unusually high RPD values while comparing duplicates to the actual results, resulting in disingenuous calculations. As such, some data that was found to exceed the warning and critical levels were judged to be valid for presentation. Percent recovery results were proven to be valid when the measured spikes were between 80% - 120%. HAA5 results sent to Advanced Environmental Laboratories, Inc. (Altamonte Springs, Fl) and carbon results from

Calgon Carbon laboratory (Moon Township, Pa) were also deemed valid as they corresponded to current National Environmental Laboratory Accreditation Program (NELAC) standards and/or state certification programs where applicable, per technical reports provided by the associated laboratories.

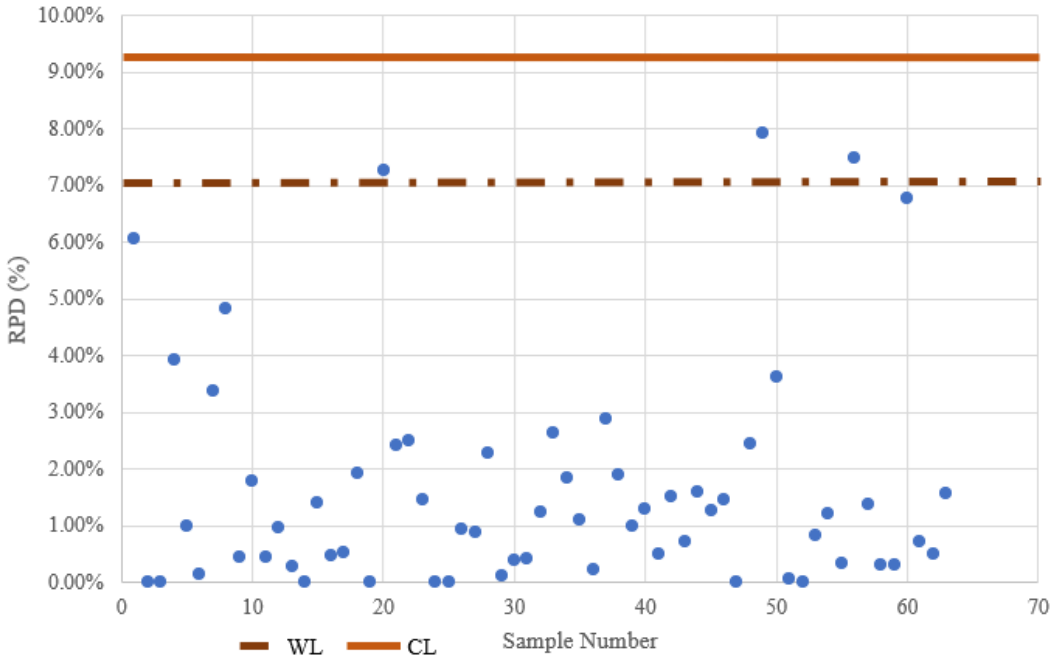

Figure 5-32: Precision Control Chart for DOC Results of the Integrated Ozone-GAC Study

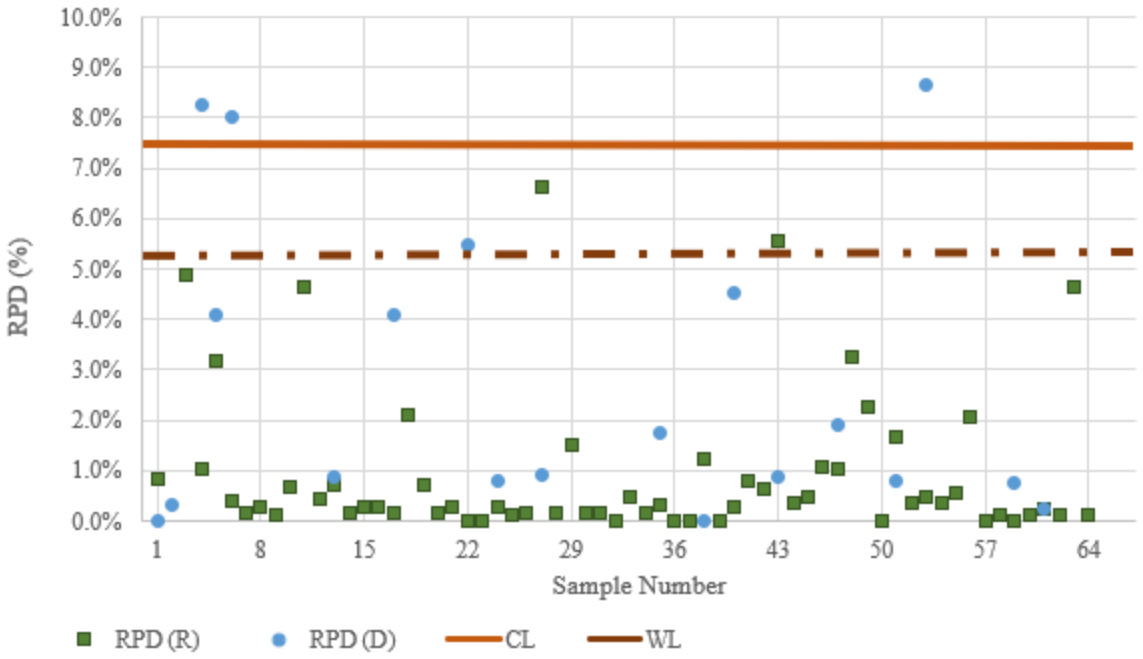

Figure 5-33: Precision Control Chart for UV_{254} Results from the Integrated Ozone-GAC Study

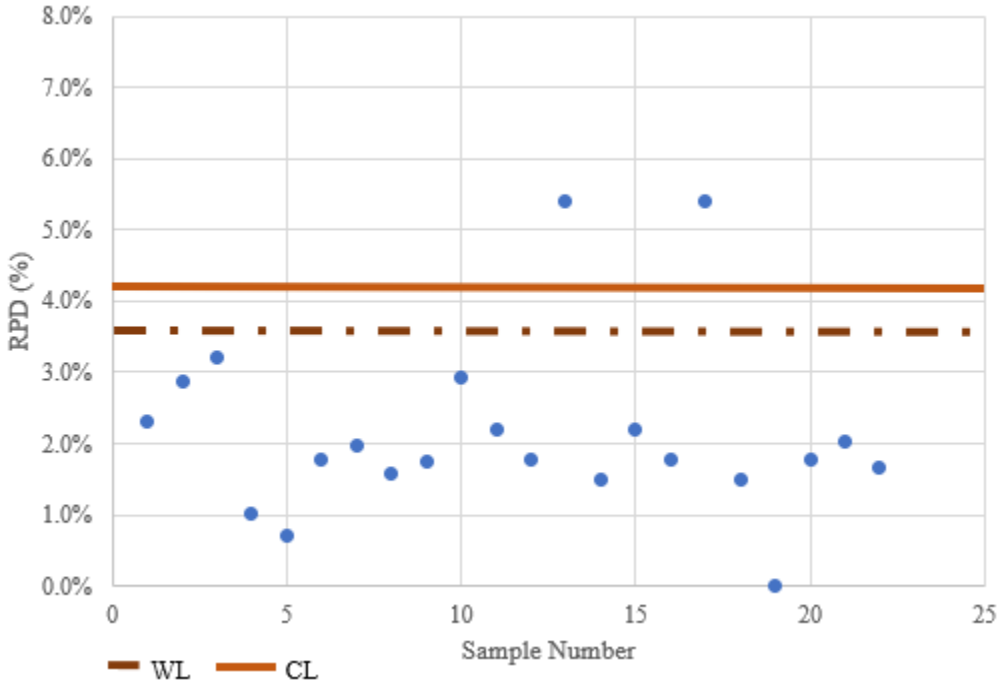

Figure 5-34: Precision Control Chart for TTHM Results from the Integrated Ozone-GAC Study

Table 5-11: Historical TTHM Percent Recovery data for the Integrated Ozone-GAC Study

Sample and Date	TTHM (ppb)	Spike (ppb)	Recovery (%)
Column A 48 (1/13)	38.5	245	103
Column A 48 (1/15)	47.6	236	94
Column B 48 (1/15)	59.9	234	87
Column A 48 (1/27)	64.0	236	86
Column B 48 (1/27)	69.0	270	101
Column B 24 (2/8)	57.0	262	103
Column B 24 (2/24)	49.0	261	106

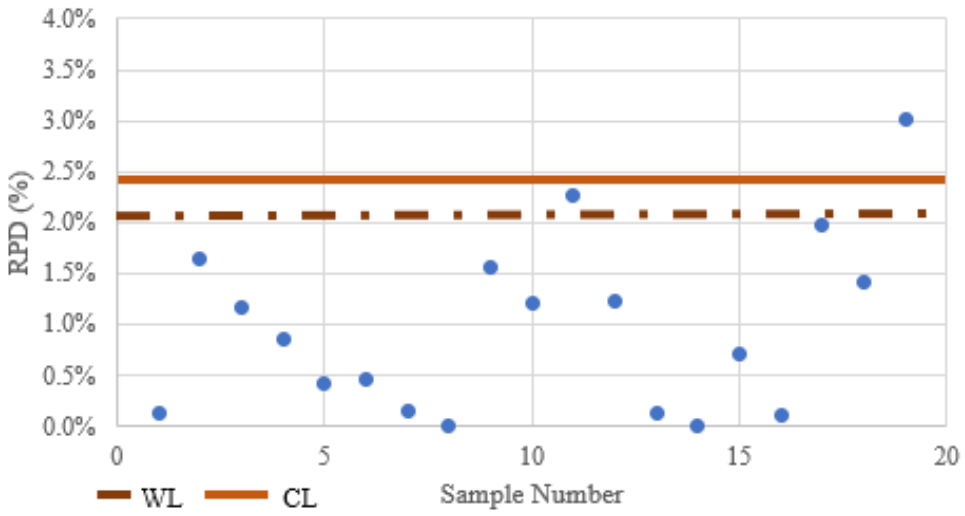

Figure 5-35: Precision Control Chart of TTHM Dupes from the Stand-alone Ozonation Study

Table 5-12: Historical TTHM Percent Recovery data from the Stand-alone Ozonation Study

Sample and Date	TTHM (ppb)	Spike (ppb)	Recovery (%)
Ozone #2 24hr (1/27)	76.6	270.6	97%
Ozone #3 24hr (1/27)	71.2	251.7	90%
Ozone #4 48hr (2/3)	86.3	271.0	92%
Ozone #5 48hr (2/5)	83	279	98%
Ozone #1 24hr (2/25)	78.4	283.2	102%

Table 5-13: Historical UV254 RPD from the Stand-alone Ozonation Study

Sample and Date	UV254 (cm^{-1})	Replicate	RPD (%)
Ozone #5 (February 8)	0.0181	0.0181	0.00
Ozone #5 (February 25)	0.0199	0.0198	0.50

CHAPTER 6. CONCLUSIONS

An evaluation on the efficiency of two potable water treatment processes, including a stand-alone ozonation process and an integrated ozonation and GAC filtration process, was completed. Such processes were operated and studied to determine the treatment efficiency for either process to reduce DBP precursors and minimize formations of DBPs through operation of the pilot unit installed at the UCF WTP. General conclusions and recommendations for future master planning of the UCF PWS are as follows.

DOC and UV_{254} Composition

Natural organics supplied within the UCF groundwater, as monitored through DOC and UV_{254}, varied from 1.95 mg/l to 4.51 mg/l and from 0.0641 cm^{-1} to 0.0914 cm^{-1}, respectively, and averaged 2.57 mg/l and 0.0765 cm^{-1} for either of the previously stated parameters. Analysis on the organic composition of UCF Well 3 and Well 4 completed by UCF ESEI on January 3, 2019, also as measured through DOC and UV_{254}, were 2.03 mg/l and 0.0830 cm^{-1}, respectively. These values lie within the range of DOC and UV_{254} observed during the integrated ozone-GAC study and are in agreement with historic Utility-collected water quality results.

Implementation of the stand-alone ozonation study upon the UCF groundwater was determined to be effective in degrading its incoming fraction of UV_{254} absorbent NOM and ineffective at reducing its incoming DOC fraction of NOM. As compared to source water conditions, the lowest dose of ozone reduced levels of DOC and UV_{254} by 4% and 61%, respectively, while the highest dose of ozone reduced levels of DOC and UV_{254} by 18% and 78%, respectively. Performance for the lowest and highest doses of ozone trial to reduce NOM from the source water was found to be

unacceptable, as more than half of the UV_{254} and a small portion of DOC was degraded by the either ozone dosage. Additionally, a higher dose of ozone than those trialed in this study was required to further reduce DBP formation would cause the utility to incur higher O&M costs, making a stand-alone ozonation process unaffordable. As such, further exploration on a stand-alone ozonation process was not pursued.

NOM treatment by the integrated treatment process proved to effectively reduce the amount of DBP precursors supplied in the UCF groundwater source. This was completed through use of an applied dose of approximately 7.2 mg/l O_3, resulting in approximately 0.37 mg/l O_3 residual. As such, a dose of ozone ample to break through the chemical demand of the groundwater supply resulted in sufficient NOM degradation. Ozone oxidation of the groundwater supply also allowed for an improved performance of NOM reduction by the pilot-scale GAC pilot columns as compared to the existing conditions and a prior GAC pilot study conducted by ESEI at the UCF WTF revealed that ozone oxidation enhance precursor removal.

Comparatively between the two piloted carbon types, the HPC-830 carbon column proved to be more efficient in reducing DOC while the FS-400 carbon column was more efficient in reducing UV_{254} absorbent organics. If operated continuously, the HPC-830 and FS-400 pilot columns would exhaust for DOC breakthrough at approximately 35,000 EBVs and 30,000 EBVs, respectively. The HPC-830 and FS-400 pilot columns would also exhaust for UV_{254} breakthrough at an estimated 25,000 EBVs and 40,000 EBVs, respectively. However, these estimates are based on the data collected for the pilot operations period. The operating times on these analogous studies are longer, and after the beds were biologically active; it is not clear as to whether the UCF pilot beds had transitioned to a full biological mode. It is noted that the DBP formation potentials did level off at the end of the study, which could be indicative that the beds may have been in the

process of transitioning to biological mode, which would possibly extend projected EBVs. The DOC exhaustion approximation projected in this evaluation, although lower in projection, also align with results from studies performed by other Central Florida potable water purveyors studying the effectiveness of an integrated ozone-GAC process to treat groundwater containing DBP precursors (Lamoureaux 2013; Reiss 2016). In those prior studies performed by the City of Sanford (Lamoureux, 2013) and Polk County Utilities Division (Reiss 2016), influent DOC exhaustion was projected to (in general) occur after approximately 50,000 EBVs.

As compared to the stand-alone ozonation process, the integrated ozone-GAC process was determined to more effective in minimizing DBP precursors from the UCF groundwater supply. The integrated process was also able to sustainably reduce both DOC and UV_{254} fractions of NOM for extended operation, which outperformed results from the stand-alone ozonation treatment study and the previous UCF ESEI stand-alone GAC treatment study.

DBP Formation Findings

As of mid-January, the UCF groundwater supply TTHM and HAA5 formation potential after incubating 48-hours at 30^{o}C averaged 95 ppb and 40 ppb, respectively. A review of DBP results from early-2021 were much lower than results presented by UCF ESEI in early-2019, where the UCF Wells 3 and 4 contained TTHM formation potentials, averaged between the two wells, at approximately 200 ppb at 48-hours of incubation. As the observed formation potential for TTHMs observed in mid-January of 2021 remain well above the MCL, a requirement for further remediation by the Utility will need to be fulfilled.

The stand-alone ozonation study was found to ineffectively minimize the formation of TTHMs, as the highest dose of ozone trialed resulted in TTHM formation that remained above the MCL for

both trials. Results from the stand-alone ozonation process indicated that the formation of TTHMs after 24-hours and 48-hours of incubation, and at an average between both trials, would be reduced from 97 ppb to 81 ppb and from 80 ppb to 65 ppb as the dose of ozone was increased. This equated to an approximate 19% and 16% reduction of TTHMs, as compared between the lowest and highest doses of ozone at 24-hours and 48-hours, respectively. Additionally, the formation of HAA5s were unaffected at lower doses and slightly increased at the highest dose of ozone. The further reduction in DBP formation through the production of an ozone dose higher than those trialed in this study was not investigated, since ozonation is highly energy intensive and the power requirement to achieve such a dose may prove to be costly to the Utility. Additionally, higher doses of ozone applied to the Utility's PWS may increase HAA5 formation profoundly, resulting in the requirement for further remediation.

The integrated ozone-GAC process successfully reduced the formation of TTHMs and HAA5s well after 50% DOC and UV_{254} breakthrough had been achieved by the pilot columns. The HPC-830 and FS-400 columns were estimated to reduce their associated TTHMs to below the MCL for approximately 22,500 EBVs and 15,000 EBVs, respectively. As expected, the HPC-830 carbon type's affinity to efficiently reduce the DOC fraction of NOM present in the supply after ozone oxidation allowed the carbon to also actively minimize the formation of the DBP for an extended period of time, as compared to the FS-400 pilot column which more efficiently treated for the UV_{254} fraction of NOM and was found to exhaust for TTHMs much sooner. In relation to the influent stream, the HPC-830 column removed 44% of TTHMs and 38% of HAA5s at 48-hours of incubation, while the FS-400 column removed 40% of TTHMs and 26% of HAA5s at 48-hours of incubation for the final 1000 EBVs of the study.

As compared to the stand-alone ozonation treatment process, the integrated ozone-GAC treatment process was again determined to be effective in reducing the formation of TTHMs and HAA5s from the source waters. As related to the TTHM formation of the UCF groundwater supply, TTHM reduction by the integrated treatment process for the HPC-830 and FS-400 carbon types outperformed results obtained by the ozonation treatment processes by about 20% at 7,000 EBVs of treatment.

CHAPTER 7. RECOMMENDATIONS

Given the results derived from the integrated ozone-GAC pilot study, it was recommended to the UCF Utility that future master planning for potable water treatment processes on campus should include an integrated ozone-GAC treatment process. If the scenario were to be chosen, then it would also be recommended to the Utility that the exploration on the installation of an additional reservoir before the GAC process and ozonation process to contain pre-ozonated supplies also be pursued. This suggested reservoir would require a contact time equal to the ozone decay rate of the supply, which was estimated to be no more than 30-minutes and no less than 10-minutes. This would allow for the oxidation capacity of the flow to be minimized before reaching the GAC process, prolonging the life of the carbon within the GAC contactors and possibly lowering the carbon replacement frequency. Carbon results support this recommendation, as it was shown that the oxidative capacity of the pre-ozonated flow that was loaded into the GAC pilot columns lowered the hardness of the tops and bottoms of the HPC-830 and FS-400 carbon types by 24% and 9.5%, respectively.

It is also recommended that the Utility explore a design concept that allows for operation of an integrated ozone-GAC process of treatment to include full-scale GAC contactors arranged in a series configuration. A series configuration typically includes a lead and a lag contactor which includes two contactors on-line and in series during operation. The primary bed, or “worker bed”, operates in the position of lead vessel and removes most of the DBP precursors fragments produced by the ozonation process, usually to acceptable levels, just by itself. The second bed, or “polisher vessel”, acts as the lag vessel and provides a safeguard against premature breakthrough or exhaustion from the worker bed. The primary unit can be taken off-line at the first hint of breakthrough leakage, or at a preset level of breakthrough leakage (i.e., 50% of inlet

concentration), or at total exhaustion (inlet contaminant level equals effluent level). Once taken off-line, the vessel may be rebedded and placed into the polisher position. The design of such a system should incorporate the proper appurtenances, piping, valves, and connections to allow the switching of the worker and polisher vessels when needed. Additionally, it would be important to consider the underdrain and header systems available for use in GAC vessels now provided on the market, as new and improved designs allow for improved flow distribution. The underdrain system controls the distribution of flow entering and exiting the vessel, and consistent and uniform distribution of flow is required during operation of the GAC vessels. If improper underdrain and header systems were to be implemented, then poor flow distribution may result in faster breakthrough and increased media usage rates and channeling may also occur if large filters are operated too slowly. To assist in distributed flow conditioning, internal cone distributors are available on the market which provides for an improved media utilization. Figure 7-1 displays an engineer drawing of an activated carbon adsorber vessel with a conical distributor in use at Polk County Utilities Division's Central Regional Water Producing Facility that treats central Florida groundwater using an integrated ozone-GAC process.

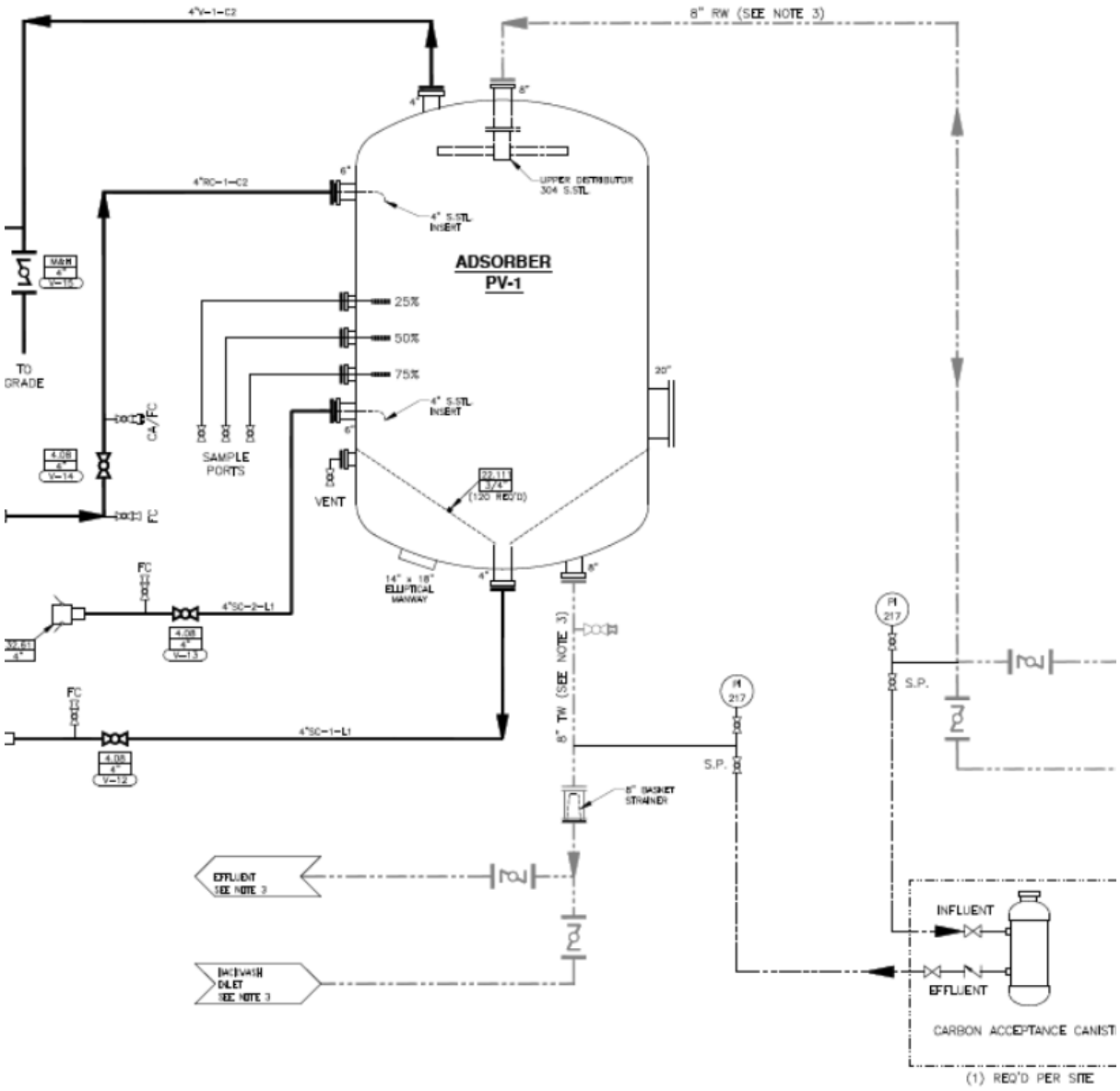

Figure 7-1: Example of an Engineered GAC Vessel with an Internal Cone Distributor

Source: Polk County Utilities Division, Winter Haven, Florida.

APPENDIX. WATER QUALITY RESULTS

Table A-1: Water Quality Results for the Combined Ozone-GAC Pilot DBP Experimentation

Dosing Date	Sample	Initial Chlorine Dose (mg/L Cl_2)	Free Chlorine (mg/L Cl_2)			pH			Temperature (°C)			Turbidity (NTU)		
			0-hr	24-hr	48-hr	0-hr	24-hr	48-hr	0-hr	24-hr	48-hr	0-hr	24-hr	48-hr
November 23, 2020	Skid	5.25	2.90	-	0.63	7.52	-	7.79	29.0	-	26.7	1.02	-	0.10
	HPC	3.00	1.62	-	1.09	7.39	-	7.59	29.9	-	27.1	0.23	-	0.12
	F400	2.75	0.95	-	0.27	7.37	-	7.68	29.9	-	27.1	0.29	-	0.15
December 21, 2020	Skid	5.25	2.28	-	0.73	7.69	-	7.69	28.7	-	28.7	0.47	-	0.47
	HPC	3.00	1.34	-	0.26	7.71	-	7.71	29.0	-	29.5	0.26	-	0.28
January 13, 2021	Raw	7.50	2.94	-	0.37	7.57	-	8.27	21.6	-	27.5	0.36	-	0.10
	Skid	5.00	2.00	-	0.25	7.64	-	7.71	25.4	-	26.1	0.13	-	0.08
	HPC	5.00	2.22	-	1.65	7.47	-	7.64	25.5	-	26.4	0.12	-	0.09
	F400	5.00	2.68	-	1.26	7.46	-	7.76	26.1	-	26.7	0.17	-	0.13
January 15, 2021	Skid	5.25	2.76	1.64	0.85	7.65	-	7.63	25.7	-	27.4	0.25	-	0.12
	HPC	3.75	2.40	2.60	1.83	7.45	-	7.51	26.0	-	27.6	0.11	-	0.10
	F400	4.75	1.52	0.99	0.79	7.52	-	7.56	25.8	-	26.6	0.12	-	0.08
January 18, 2021	Raw	7.50	2.98	0.67	0.53	7.49	-	8.16	18.8	-	27.5	0.68	-	0.12
	Skid	5.25	2.12	0.76	0.53	7.61	-	7.63	24.6	-	25.0	0.31	-	0.21
	HPC	3.75	1.62	0.92	0.76	7.47	-	7.59	24.4	-	25.7	0.15	-	0.10
	F400	3.75	1.64	0.66	0.59	7.49	-	7.68	24.5	-	25.6	0.15	-	0.12

Dosing Date	Sample	Initial Chlorine Dose (mg/L Cl_2)	Free Chlorine (mg/L Cl_2)			pH			Temperature (ºC)			Turbidity (NTU)		
			0-hr	24-hr	48-hr	0-hr	24-hr	48-hr	0-hr	24-hr	48-hr	0-hr	24-hr	48-hr
January 27, 2021	Skid	5.25	3.08	1.16	0.43	7.41	7.75	7.70	27.4	25.2	25.7	0.57	0.11	0.12
	HPC	4.25	2.74	1.54	1.50	7.42	7.61	7.70	28.2	26.4	27.4	0.18	0.08	0.08
	F400	4.25	2.58	1.34	1.08	7.47	7.63	7.41	27.5	26.5	26.8	0.17	0.09	0.12
February 8, 2021	Skid	5.00	2.68	0.98	0.67	7.58	7.69	7.61	25.1	28.1	27.1	0.45	0.12	0.11
	HPC	3.75	2.14	1.36	1.09	7.43	7.65	7.60	25.5	28.1	27.8	0.17	0.11	0.15
	F400	3.75	2.14	1.04	0.80	7.45	7.66	7.26	25.3	27.8	27.0	0.11	0.10	0.10
February 15, 2021	HPC	3.75	2.18	1.38	1.00	7.33	7.66	7.63	26.8	26.2	26.4	0.16	0.14	0.13
	F400	3.75	2.36	1.63	1.44	7.36	7.56	7.65	27.2	26.0	26.6	0.13	0.13	0.12
February 24, 2021	HPC	3.25	2.08	1.28	1.13	7.31	7.54	7.51	26.9	26.8	27.2	-	0.27	0.14
	F400	3.25	1.69	1.13	0.92	7.33	7.59	7.58	26.8	27.8	28.1	-	0.14	0.15

Table: A-2: Water Quality of Stand-alone Ozonation DBP Experimentation

Dosing Date	Sample	Initial Chlorine Dose (mg/L Cl_2)	Free Chlorine (mg/L Cl_2)			pH		Temperature (^oC)		Turbidity (NTU)	
			0-hr	24-hr	48-hr	0-hr	48-hr	0-hr	48-hr	0-hr	48-hr
January 27th, 2021	#1	5.00	2.62	0.88	0.64	7.41	7.80	27.4	25.7	0.57	0.12
	#2	5.00	2.90	0.98	0.70	7.78	7.78	24.5	25.8	0.35	0.11
	#3	5.00	2.98	1.10	0.70	7.75	7.76	24.9	26.2	0.42	0.25
	#4	5.00	2.92	1.22	0.88	7.69	7.61	21.6	27.2	0.20	0.10
	#5	5.00	2.84	1.50	1.16	7.68	7.80	27.2	27.2	0.13	0.13
March 1st, 2021	#1	5.00	2.78	0.92	0.66	7.58	7.76	26.8	26.8	0.18	-
	#2	5.00	2.86	1.06	0.71	7.49	7.58	27.3	27.5	0.33	-
	#3	5.00	2.80	1.19	0.81	7.41	7.56	25.8	27.5	0.35	-
	#4	5.00	3.28	1.34	0.98	7.50	7.49	27.5	27.4	0.89	-
	#5	5.00	2.92	1.31	0.97	7.49	7.43	26.4	27.3	0.26	-

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